Electrochemical and Metallurgical Industry

NEW YORK, SEPTEMBER, 1907.

CONTENTS.

Announcement.

After Sept. 1 the offices of this journal will be removed to the new "Thirty-ninth Street Building," 239 West Thirty-ninth Street. This location is in the heart of what is predestined to become a most important business center of New York City after the completion of the various tunnels and the new Pennsylvania Railroad station. Our friends will enjoy being able to reach us in a three minutes' walk from the United Engineering Building or the Engineers' Club, or in some fifteen minutes from the Chemists' Club. The building itself is interesting from an engineering standpoint as the most important reinforced concrete office building on Manhattan Island.

Prices of the Metals in the Fall.

As we predicted last winter, the price of copper has taken a tumble; 25-cent copper was altogether too high, and nothing warranted the continuation for a long time of the price of metals at such figures. It was restricting consumption. As nobody will buy in a falling market, the copper market exhibits a most plastic condition. It has been "punched" hard by the offering of the smaller mining and smelting companies who have a fat margin at present prices, and also by the large custom smelters who have to sell the copper from a number of small producers of ore. It is doubtful if the larger companies who are trying to hold up the price can continue to accumulate stocks of metal. It should be remembered that they had an unfortunate experience in 1901, when the same thing was attempted. It should also be remembered that present prices are even higher than in 1901, when the big producer tried to hold the umbrella over the market.

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Pig iron and steel products are selling on old orders, but there also appears the same deadlock between producer and consumer. The wise policy of the dominating interest in holding down prices in 1906-7 below prices of 1902 prevented a runaway market. Lead, of course, is sold on quotations made by the "trust," and its price is largely artificial, especially as same interests are largely interested in the consuming companies. The spelter market has been distressingly weak, and spelter soon will be selling at prices where neither mine owner nor smelter can make a dollar. The free competition in this field, however, has caused the drop to such a price, that cost of production fixes the price of metal rather than monopolistic control. It is probable that the reaction has been a good thing for business, for high prices surely throttle consumption. When prices react and people recover from the hysteria that a falling market always engenders, we see no reason for fear that political disturbances of the presidential year will do any more than slow down business to a normal basis.

Combustion and Dissociation.

It was a favorite mode of expression—and is still commonly used—to say that the temperatures attained by ordinary combustion are limited because of the dissociation of the products of combustion as high temperatures are reached. We opine that most books on combustion, even at the present moment, are continuing to spread this erroneous view. The facts are, that if CO_2 and H_2O do dissociate to anything like the extent which St. Claire Deville and other early experimenters on dissociation believed, then our furnace temperatures are seriously kept down by that dissociation. But that idea has been repeatedly shown to be false, yet it dies hard. Water vapor and CO_2 dissociate to such an inappreciable extent at all ordinary furnace temperatures that the effect on the resulting temperature is in reality negligible. Langmuir published in the last volume of the *Journal* of the American Chemical Society (XXVIII., 1,358-1,379) a very laborious determination of the dissociation of H_2O vapor and CO_2, finding them to be, at 1,000° C., dissociated to the extents of 0.003 per cent and 0.004 per cent respectively; at 1,500° C. to 0.17 and 0.55 per cent, and even at 2,000° C. to the extent of only 1.3 and 5 per cent. It follows, that wherever a fuel containing carbon and hydrogen is burned, the dissociation of the products by their own self-generated high temperature does not check that temperature more than 0.05° C. at 1,000°, or 9° C., at 1,500° C., or 50° to 100° at 2,000°. Since our open-hearth furnace roofs commence to melt at 1,750°, we are not in practice suffering at all from low temperatures produced by supposed dissociation of H_2O and CO_2. Let us revise our modes of speech and talk according to present known facts.

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Fixation of Atmospheric Nitrogen.

In our April issue, 1906, we referred to a certain scheme of producing ammonia from nitrogen of the air, on the basis of the property of certain elements to combine comparatively easily with nitrogen. Thus lithium forms a nitride according to the equation $3Li + N = Li_3N$. By treating the nitride with water it is then possible to get ammonia with the simultaneous formation of lithium hydroxide. The lithium is, of course, intended to be employed simply as a carrier for the nitrogen, and is to be used over and over again. To make the process cyclic, with respect to lithium, it becomes necessary to regenerate the lithium from the hydroxide. This could be done by electrolysis. But the whole process is undoubtedly too complicated and expensive to be attractive. In our present issue we publish a paper by Mr. Norman Whitehouse on an interesting research carried out at the suggestion of Sir William Ramsay. The intention was to try a scheme quite similar to that sketched above, but greatly simplified in so far as the nitride formed is not treated with water, but with hydrogen or water gas to produce directly ammonia and regenerate the metal.

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If practicable such a process would be delightfully simple. If we designate with M the metal which is to act as nitrogen-carrier, the two steps of the process would be $M + N = MN$ and $MN + 3H = M + NH_3$, and so on. Unfortunately, Mr. Whitehouse's experiments seem to prove conclusively—and this is the valuable result of his paper—that those elements which he tried do not behave like our hypothetical metal M.

The trouble is that with real metals we may be able to produce either the first or the second reaction, but not both together. Metallic nitrides may be directly reducible to form ammonia, but such nitrides cannot be directly produced from the elements. Other nitrides may be made directly from the elements, but are not directly reducible. Thus, although very attractive, this scheme seems not capable of realization, and we are thrown back on electrical methods for the fixation of atmospheric nitrogen.

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The paper of Mr. F. Howles, of which we publish a long abstract in this issue, gives an interesting résumé of the chief processes employing electric discharges through air. Mr. Howles, who has been himself an early worker in this field, shows clearly the points in which the early experimenters failed. Mr. Howles is on the solid ground of the physico-chemical theory that the effect of the arc or spark discharge is simply thermal. We have to do with an electric furnace process. We thus have the two well-known requirements that we need as high a temperature as possible in the active zone of the arc, and that we must remove the gas mixture from the sphere of influence of the arc so quickly as to prevent dissociation in the cooler parts of the arc. But Mr. Howles adds another important consideration for a commercial process, namely, that it is necessary to concentrate as large an amount of energy in a unit of plant as possible to keep maintenance and labor charges down. It was in this point that the early processes failed. This is very important, since we have two main expenses which cannot be avoided, one is the expense for the electrical energy, the other the expense for working up the end product of the electric furnace process—a mixture of gases containing somewhat like 2 per cent of nitric acid into a marketable product.

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Because the Birkeland-Eyde process is commercially successful in Norway, we like to speak of the problem as solved, which is correct to a certain extent. But it is significant that the process does not appear to make much headway elsewhere. The fact is that the very cheap power in Norway (somewhat like $5 per horsepower-year) represents a very special condition. These Norwegian conditions cannot be duplicated in this country, and if we could get power so cheaply it would probably pay better in most localities to utilize it for other purposes. However, it would seem that the process has not yet reached finality, and we may expect that the persistent and indefatigable work of the Norwegian pioneers will succeed in further reducing the cost of the process. In the meanwhile the other process of fixing atmospheric nitrogen—the manufacture of calcium cyanamide—is gradually extending from the pioneer plant in Italy into other countries. Thus, in this country a plant is planned for the South. The two chief items of the cost are here the raw materials: the calcium carbide and the nitrogen, which must first be separated from the oxygen in the air. The calcium cyanamide manufacture itself is simple. We have not heard of the special method which will be used in the Southern plant to separate the nitrogen from the oxygen in the air. In the Italian plant distillation of liquid air is reported to be employed. It is perhaps significant that the manufacture of liquid air apparatus is just now entering into the commercial stage in this country.

Again the Corrosion of Iron.

The two papers of Dr. Walker and Dr. Cushman, published elsewhere in this issue, give us an opportunity to add some further comment to our remarks in the July issue. We have now three important hypotheses on the causes of corrosion of iron. The carbon dioxide theory, originally proposed by Grace Calvert and Crum Brown, and now strongly defended by Mr. Moody, assumes that the corrosion of iron proceeds in two steps, the first of which assumes the presence of carbon dioxide. The equations of the two reactions are: (1) $Fe + H_2O + CO_2 = FeCO_3 + H_2$ and (2) $4FeCO_3 + 6H_2O + O_2 = 2Fe_2O_3(H_2O)_3 + 4CO_2$. Hence, in the second step carbon dioxide is reformed, which then acts on fresh iron, and so on. The hydrogen peroxide theory also assumes that the corrosion of iron proceeds in two steps, of which the first is the formation of hydrogen peroxide by the reaction (3) $Fe + O_2 + H_2O = FeO + H_2O_2$, while the second step is the action of H_2O_2 on Fe and FeO, according to the equations (4a) $Fe + H_2O_2 = FeO + H_2O$ and (4b) $2FeO + H_2O_2 = Fe_2O_3(H_2O)$. The electrolytic theory, originally proposed by Dr. W. R. Whitney and now so ably defended and further developed by Dr. Cushman and Dr. Walker, assumes that when an iron surface is in contact with moisture, which may act as an electrolyte, differences in the composition of the iron will result in making some parts of the iron surface anodes and other parts cathodes. Thus, we have short-circuited galvanic cells. At the anode the iron will pass into solution, assuming the ferrous ionic state, while hydrogen is liberated at the cathode, the equation being most easily expressed in the notation of the ionic theory (5) $Fe + 2H^{\cdot} = Fe^{\cdot\cdot} + H_2$. For those who object to the electrolytic dissociation theory, this equation will mean nothing more than that one free iron atom gains two bonds, while simultaneously two monovalent hydrogen ions lose each one bond; expressed in this way the equation cannot be objectionable to anybody. The second step is the oxidation of the ferrous ions to ferric by oxygen of the air. The equation may tentatively be written (for argument's sake, although it is not the most general form) (6) $2FeA + (x + 2)H_2O + O = Fe_2O_3(H_2O)x + 2H_2A$, where A stands for any bivalent anion. Here the two bivalent Fe atoms on the left-hand gain each one positive bond and become threevalent, while the one free O ion on the left-hand gains two negative bonds. The loose colloidal ferric hydroxide moves towards the cathode under the influence of the current and piles up there in form of rust.

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It is unnecessary to emphasize the differences between the three theories. It seems more useful to point out how far they agree. All three theories agree that the oxidation of iron by oxygen of the air is not direct, and in this point they agree clearly with all experimentally established facts. Further, all three theories agree that the formation of rust proceeds in essentially two steps, of which the first step is the passing of the free metallic iron into the bivalent state, and that the formation of rust is a subsequent second step, involving the change from the ferrous to the ferric state. According to the carbon dioxide theory, the first step is the change of Fe to $FeCO_3$, a bivalent compound; according to the hydrogen peroxide theory the change is from Fe to FeO, also a bivalent compound; while the electrolytic theory simply claims the metallic iron to pass into solution and get bivalent. Evidently the electrolytic theory which leaves the question of the anion entirely open is the more general theory, and in this respect it comprises the other two theories as special cases, representing possible, but not necessary, reactions. The adherents of the electrolytic theory cannot deny that when iron is in contact with carbon dioxide, water and oxygen, the reactions claimed by the carbon dioxide theory will occur; but they deny that it is by means of these special reactions that rust is formed in general, and Dr. Cushman's and Dr. Walker's repetition of Mr. Moody's experiments appear to offer conclusive evidence in favor of their theory. Viewed from the standpoint of the electrolytic theory, the carbon dioxide theory emphasizes one single possible anodic reaction, namely, the change of iron into ferrous carbonate. On the other hand, the hydrogen peroxide theory seems to emphasize to a certain extent one single possible cathodic reaction, if we follow the interesting suggestion of Dr. Walker. It was found by Richarz and Lonnes that the electrolysis of water saturated with air is possible at a relatively low electromotive force, because the air in the water acts as a depolarizer at the cathode, so that the cathodic product is not hydrogen gas but hydrogen peroxide. If hydrogen peroxide can exist at an iron surface, we should expect it to be formed at such spots of the iron which act as cathodes, and this formation (on account of the lower potential compared with hydrogen gas development) would accelerate the passing of iron from the anodic areas into the ferrous ionic state.

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While the subject is of highest theoretical interest, it is of no less practical importance. What can be done to overcome the innumerable troubles due to corrosion of iron? Surely Dr. Cushman's suggestion to try treatment with bichromate solutions on a large scale deserves fullest attention. It should be noticed that Dr. Cushman is exceedingly careful and conservative in his predictions, yet he concludes: "Although it is true that laboratory tests are frequently unsuccessful in imitating the conditions in service, it, nevertheless, appears that chromic acid and its salts should under certain circumstances come into use to inhibit extremely rapid corrosion by electrolysis." However, we should not overlook that such treatment is somewhat like treating a sick person continually with medicines and nursing him along in such a way without restoring him really to health. The fundamental trouble in the corrosion of iron lies in the iron itself, in its non-uniformity. Treatment with chromic acid has only a temporary superficial effect and does not change the composition of the iron. The radical cure to prevent corrosion of steel would be to make better steel, "as free as possible from certain impurities, such as manganese, and so homogeneous as not to retain localized positive and negative nodes for a long time without change." This is quoted from Dr. Cushman, with whom we fully agree, but we may add again what we already pointed out in the July issue, that according to the present state of art it is quite possible that the cheapest way to do this might be to treat open-hearth or Bessemer steel subsequently in the electric furnace. If the corrosion of iron is an electrolytic process and electrochemistry is at the bottom of the corrosion trouble, it would be only proper that another branch of electrochemistry —the electric furnace—should solve the problem.

The Iron and Steel Market.

The extreme dullness in the market in July has been carried through August. There has been substantially no buying of pig iron, while in finished material there has been very little in the way of entering into absolutely new engagements; there has been a fair, but only fair, run of specifications and orders against old contracts.

The trade has exhibited a new phenomenon; through this extreme market dullness production has kept up to the physical limits. Never before has such a period of market dullness failed to make an impress upon actual production, and the present outcome is a testimony to the soundness of the contract obligations which the furnaces and mills had on their books at the end of the second quarter.

It is true production has declined slightly, but this was due entirely to the hot summer weather. Pig iron production has declined slightly, but less than it usually does in mid-summer, as several new furnaces have been blown in. Practically all the pig iron has gone into consumption, and the steel in turn has been rolled into finished forms and shipped. The accumulations of foundry pig iron at furnaces and in consumers' yards has been very slight.

It is a question now whether or not a genuine fresh buying movement will be inaugurated in time to save the situation or, failing this, how long the present obligations will permit of full activity. The prospects of a heavy buying movement are far from favorable. It is found that money is really tight, and there is no good reason to believe that the much-heralded retrenchment policy of the railroads will be abandoned. It certainly looks as if general business would have to be conducted on a somewhat reduced plane, as to both prices and volume. The financial world seems to have been going on the basis for several years that the increase in the gold production meant an equal increase in the amount of gold available as money; now that conditions require a more careful scrutiny it is developed that the supply of money has not increased half as much as has the production of gold, a fact which men could have discovered before had they taken pains. As to the railroads' retrenchment policy, the Southern Railway has reduced its preferred dividend, making a statement that the reduction is due to higher costs, and Wall Street judges that some other roads will have to make dividend reductions. These things do not augur for liberal expenditures for iron and steel products on the part of the railroads.

Events have shown the justice of our remarks a month ago on the strike at Lake Superior ore docks and mines. The strike ended after a total loss in shipments of 2,000,000 or 3,000,000 tons, at the outside, and it is now certain that all the ore which will be needed can still be brought down.

Pig Iron.

There has been no buying except of occasional small lots for early shipment. Prices on such transactions have been from 50 cents to a dollar lower than the market two months ago for deliveries late in the year. For such late delivery there is now no market at all, so that similar deliveries cannot be compared. The United States Steel Corporation bought 15,000 tons of Bessemer for August delivery, paying $22, valley furnace, equal to $22.90, delivered Pittsburg, or 50 cents less than had previously been done on any delivery. It is extremely unlikely that it will buy any September iron, as it will not need it, and would not want to support the market, as it would prefer to see lower prices on Bessemer pig. The Cambria Steel Co., which has been getting about 10,000 tons a month from the open market, has blown in its new No. 8 furnace, and will not require outside iron after Sept. 1. This will throw 25,000 tons or more of Bessemer pig on the market, and lower prices appear inevitable. In basic pig it has been impossible to move the iron which has been offered for

some time, and with the blowing in of the Inland Steel Co.'s new furnace the iron it has been taking will also have to be disposed of. Basic has been nominally $21, valley, but there is no question that this price could be shaded.

In foundry pig iron a condition of extreme apathy prevails. Deliveries are pretty well taken but there is no interest whatever in future deliveries. Prices are purely nominal, as there is nothing to test the market. Nominally No. 2 foundry can be quoted at $22, valley furnace, or $22.90, Pittsburg, and forge $1 to $1.50 less.

Steel.

The purchases of billets by the United States Steel Corporation, made through its subsidiary, the Carnegie Steel Co., are being continued at intervals. During the second quarter 56,000 tons were bought, and during July 30,500 tons, while in August a smaller quantity was taken. Prices are fairly well maintained considering the lack of interest. Bessemer billets can be had at $29, maker's mill, or perhaps a trifle less, and open-hearth billets at about $30, maker's mill. A number of mills are not sellers at all.

Finished Material.

Nothing new has been developed in the situation as to specifications for rails for 1908 delivery. The committee will meet some time in September. The mills are well filled up for the current year.

Throughout the finished steel trade mills are well filled with specifications and can run at full capacity for some time yet. In sheets there is some strictly new business, while orders and specifications on old contracts are excellent. In steel bars conditions are about the same as in sheets. In plates and shapes there is very little absolutely new business, but fairly good specifications. Prices are unchanged, except that iron bars are slightly easier, and are quotably lower for Pittsburg delivery. Prices are as follows, f. o. b. Pittsburg:

Structural shapes, $1.70 per 100 pounds for beams and channels, 15 inches and under.

Plates, $1.70 for tank quality.

Merchant steel bars, $1.60, base.

Common iron bars, $1.70, delivered Pittsburg, and $1.60, f. o. b. Pittsburg, for Western delivery.

Sheets, 28 gauge, $2.60 for black and $3.75 for galvanized.

Tin plates, $3.90 for 100-pound cokes.

A New Steel Process.

In our July issue, page 279, and in our August issue, page 322, we have already noticed two patents granted to Mr. Horace W. Lash for a new electric steel process, and in the Analysis of Current Electrochemical Patents in our present issue an abstract will be found of a third patent granted to Mr. Lash.

Mr. Lash is the vice-president of the Garrett-Cromwell Engineering Co., of Cleveland, and for the introduction of his steel process into practical use the Lash Steel Process Co., of Cleveland, Ohio, and the Canadian Lash Steel Process Co., Ltd., of Toronto, Ont., have been formed. The general offices of both companies are in the White Building, Buffalo, N. Y., Mr. Seward Babbitt (formerly with the De La Vergne Machine Co.) being secretary and general manager.

The chief claim made for the process is that it produces steel of good open-hearth quality from a mixture of iron oxide and pig or cast iron. The quantity of cast iron required never needs to be more than that of the iron oxide and may be considerably less, successful results having been obtained when the cast iron was not more than one-fourth of the weight of the iron oxide.

The iron oxide and the pig iron must be used in a finely

divided condition. Hence if iron ore is used it must first be crushed. The process is, however, well adapted to the direct treatment of magnetic concentrates, such as produced from the sand ores of the St. Lawrence and New Zealand or on the Pacific Coast, or from the magnetic ore mines in Northern New York and Canada. It is important to note that association of such substances as titanium oxide does not interfere with the process.

The process, therefore, appears to offer a solution of the problem which has been attacked so often in the past—the reduction of magnetic concentrates. It is interesting to compare this process with another electric process which was devised for the same purpose, that of Mr. Ruthenburg. In the Ruthenburg process the electric furnace simply serves for fritting the concentrates together into lumps, the reduction to be carried out afterwards while the lumps are hot but not molten. In Mr. Lash's process the reduction goes on while the charge is actually molten.

It has already been noted that the pig or cast iron must also be in a finely divided or shotted condition. But it is to be emphasized that it must be that quality of iron commonly designated as cast or pig iron, as distinguished from the ordinary run of scrap, wrought iron or steel, since it is important that it contains a high percentage of metalloids or oxidizable metals such as manganese, capable of uniting with the oxygen of the ore. Besides iron oxide and cast iron the charge contains carbon as reducing agent, preferably in form of ordinary coke and finely ground, also fluxes of the ordinary kind, such as lime, silica or fluorspar, varied to suit different grades of ore and the different conditions under which the mixture is melted. Finally, it is advantageous to add some sawdust or crushed bituminous coal to the charge. This is consumed during the early stage of the smelting operation, and thus leaves the mass porous so that the smelting may proceed with greater rapidity. Some figures giving the exact proportions of various mixtures suitable for smelting were given on page 322 of our August issue.

The theory of the process is as follows: The pig or cast iron in the finely divided intimate mixture with the iron oxide has a double effect. First and primarily, the pig iron contains a high percentage of metalloids and generally manganese, which are presented to the oxide in the most intimate and effective condition possible, and therefore are active and ready reducing agents. Secondly, the fused pig iron appears to act simultaneously as a solvent for some of the free carbon and as an enveloping coat for the individual particles of oxide, thus bringing the dissolved carbon into intimate association with the oxide to supplement the reducing effect of the metalloids contained in the pig iron. The free carbon should be present in sufficient quantity to insure the proper carburization of the smelted metal, so as to maintain it in a fusible condition and also sufficient to protect the mixture against atmospheric oxidation.

In extended tests of the process, using both the electric furnace and the open-hearth, it has been found that practically the entire quantity of iron contained in the oxide as well as the entire quantity of pig iron added, was obtained in the molten product, the yield averaging 96 and 98 per cent.

The trials with the open-hearth furnace have been made and are still under way at the plant of the Carbon Steel Co., of Pittsburg. Heats from 10 to 15 tons have been made, the yield averaging about 96 per cent of the metallic matter charged.

The electric furnace trials were made at Niagara Falls by Messrs. FitzGerald and Bennie. In these trials the charges were made up of one-fourth pig and three-fourths iron ore. The average yield from the metallic content charged was about 98 per cent. It is intended to test the new process in the Héroult electric furnace plant in Remscheid, Germany, and in the Stassano electric furnace in Italy. The process is also to be tested with Canadian magnetic concentrates on the Canadian side of Niagara Falls. The prediction is made that within the next few months the new companies will be able to produce by this process open-hearth steel at a cost of several dollars per ton less than is at present possible by using pig iron or pig iron and scrap.

The Detinning Suit.

On page 46 of our Vol. IV. we gave an account of the decision of Vice-Chancellor Bergen in the Court of Chancery of New Jersey, Newark, N. J., in the suit of the Vulcan Detinning Co. as complainant against the American Can Co. as defendant. The decision was in favor of the latter.

As was already noticed in our last issue this decision has now been reversed by the New Jersey Court of Errors and Appeals, the decision being delivered by Judge Garrison. Since it is a matter of great interest to see to what extent the courts go in protecting the discoverer of a secret process, we give below extended extracts from the decision, but will first give a summary of the facts in the case:

As early as 1891 the firm of Th. Goldschmidt, in Essen-Ruhr, operated an electrolytic process for detinning tinned iron scrap. A large part of the tin scrap treated was shipped to them from New York by A. Kern. The latter became impressed by the possibilities of erecting a detinning plant in this country and entered into negotiations with Goldschmidt's to get their process, but the latter declined. "In the course of this correspondence Dr. Goldschmidt had in a letter of May 16, 1896, stated that his process was being used at Vlissingen, Holland, by a concern called the Tinfabriek, which had been organized by one Laernoes, who had clandestinely obtained the secret of the process."

For a party of New York merchants and manufacturers, among them Mr. Assmann, Mr. Kern bought from Laernoes the secret of the process for $200,000, and the latter came to this country to install the first plant of what is now the Vulcan Detinning Co. Mr. Assman as a director of this company had knowledge of the secret of the process. In 1901 he resigned, having become a director of the American Can Co. Shortly after the American Can Co. began the erection of two detinning plants, using the same process. The original suit was brought by the Vulcan Detinning Co. against the American Can Co. to enjoin the latter from using the process.

We now quote from Judge Garrison's decision:

"The learned Vice-Chancellor reached the conclusion that the process used by the Tinfabriek was a fraud upon the Goldschmidt's, of which Kern by reason of his correspondence with Dr. Goldschmidt in 1896 had knowledge, and that when Kern in 1898 became the agent of the corporators of the complainant, through whom the Tinfabriek process was acquired, the prior knowledge Kern had thus casually obtained must be imputed to the complainant under the decision of this court in the case of Willard vs. Denise. Having reached this conclusion as to the imputation of Kern's knowledge to the complainant, the Vice-Chancellor further concluded that the effect of such imputation was to render the hands of the complainant unclean within that maxim of equity by which a deaf ear is turned to a suitor in a court of conscience regarding a matter in respect to which his own conduct has been unconscionable.

"In reaching this last conclusion the learned Vice-Chancellor fell, we think, into the error of ascribing an unconscionable status to the complainant by force of a presumption of remedial law that in its extreme application affects only the legal rights of parties and not at all their moral standing. That the knowledge possessed by an agent, but not acquired by

him while acting for his principal, will under certain conditions be imputed to the latter, is in the nature of a presumption indulged in by courts in working out the rights of litigating parties." * * * But "an essential part of the presumption in question is that the principal is ignorant of the knowledge that has been casually acquired by his agent; hence, by the hypothesis, the principal is not only ignorant of the knowledge thus acquired, but if such knowledge involves a fraud the principal is innocent of such fraud. True, he may be bound by it in the sense that his legal rights may be determined with reference to the knowledge with which he is thus chargeable, but his conscience is void of offense, and hence it cannot with any propriety be said that his hands are unclean; for 'unclean hands' within the meaning of the maxim of equity is a figurative description of a class of suitors to whom a court of equity as a court of conscience will not even listen, because the conduct of such suitors is itself unconscionable, i. e., morally reprehensible as to known facts."

Concerning the formation of the companies which are now the Vulcan Detinning Co., and their purchase of the secret from Laernoes, Judge Garrison says: "Of the good faith of the American corporators in the transaction which involved the payment of this large sum of money no legitimate doubt is raised by the testimony. Whether the prior knowledge possessed by Kern made his conduct fraudulent as to the Goldschmidts, so that in a suit brought by them such fraud would be imputable to these corporators, is a question that does not concern this present controversy. It should be noted, however, that there is a wide difference between the absolute secrecy which the discoverer of a process has the legal right to protect and the qualified secrecy which the complainant claims the equitable right to secure." * * *

"The main ground for relief disclosed by the complainant's case is the existence of inequitable competition arising from a breach of trust, and hence referable to general principles of equity and not to those special doctrines by which unpatented secrets are protected. In the application of these general principles the secrecy with which a court of equity deals is not necessarily that absolute secrecy that inheres in discovery, but that qualified secrecy that arises from mutual understanding and that is required alike by good faith and by good morals." * * *

"Entirely aside from the technical secrecy of the process or the abstract question of property therein, the complainant is entitled to have its trustees, his associates and their servants, restrained from using against the interests of the complainant the very process with which its trustee was entrusted for its benefit."

The question is then discussed at length whether the breach of trust committed by Assmann is chargeable to the American Can Co., and is answered in the affirmative. The criterion by which this question is to be answered is taken from an opinion of Mr. Justice Dixon in a case of the State vs. Sooy: "The knowledge of the agent is chargeable upon his principal whenever the principal, if acting for himself, would have received notice of the matters known to the agent."

Concerning the license to work the process which the American Can Co. obtained from the Goldschmidts after the bill of complaint had been filed, Judge Garrison rules as follows:

"At the time the assignment was thus taken the defendants were fully apprised by the bill of complaint, if in no other way, of the precise nature of the complainant's claim to relief. The decision we have reached carries with it the defence that is thus sought to be set up under this assignment, upon the doctrine that if a trustee purchase a title that cures or completes one that he holds in trust, the presumption in equity will be that the later purchase was made in aid of the former trust." The Court of Appeals enjoined the American Can Co., but did not order an accounting, but sent the case back to the lower court for having the question of accounting determined.

CORRESPONDENCE

Detinning with Chlorine.

To the Editor of Electrochemical and Metallurgical Industry:

Sir:—On page 339 of your September issue of 1904, Dr. F. Winteler, summarizing the possible uses of electrolytic chlorine, calls attention to the detinning of tinned iron scrap with dry chlorine. He reminds us of the well-known behavior of dry chlorine gas on tin and iron at temperatures not exceeding 100° C., and proposes a process of detinning.

On Aug. 1 of the same year, F. von Kügelgen and G. O. Seward filed an application for a patent on a process of detinning with dry chlorine gas in an anhydrous solution, e. g., stannic chloride. This patent (U. S. patent 783,726) was granted on Feb. 28, 1905. On May 29, 1906, Karl Goldschmidt and Josef Weber obtained a patent (U. S. patent 822,115) on practically the same process. This patent was followed by a second granted to the same petitioners on Sept. 16 of the same year (U. S. patent 831,223). The last-named patent protects a process of detinning tin scrap with dry diluted chlorine gas under altering pressure.

The fact that Dr. Karl Goldschmidt, member of the firm Theodor Goldschmidt, which operates so successfully the electrolytic process for detinning tin scrap, was engaged in experimenting on a purely chemical detinning process, called general attention to the chlorine detinning process. The knowledge of the fundamental reactions of these detinning processes with dry chlorine is very old. Not so well known, but probably of great interest to some of your readers, is the fact that chlorine detinning was already practiced in Europe on a commercial scale as early as 1873.

Prof. G. Lunge, describing the exhibition of the chemical works of Gebrüder Schnorf, Uetikon, in his *Bericht über Die Chemische Industrie auf der Schweizerischen Landesausstellung, Zürich,* 1883 (a report not easily accessible), writes on page 29:

"Very interesting is the process of detinning tin scrap. This process takes advantage of the inability of dry chlorine to attack iron, while it dissolves tin to stannic chloride. A cylinder, 1 meter in diameter and 4 meters high, has a tipping grade above the lower bottom on which the scrap rests. The chlorine gas enters underneath the grate and the fuming stannic chloride collects in a bottle placed underneath the cylinder. When the flow of tin chloride ceases the operation is stopped, the bottle and the underbottom are removed and the grate is tipped to remove the iron. The process may then be repeated as before. The tin scrap comes mostly from Cham, where tin cans are made on a very large scale for condensed milk.

"There is scarcely any commercial use for stannic chloride as such, but converted into solid chloride by judicious mixing with water and then further dissolving to solutions from 50° to 60° B., it is extensively used in silk dye factories. Since direct resmelting is not practiced in Switzerland, the iron is converted into sulphate of iron, of which 1,100 tons are produced yearly.

"It is very desirable that another use be found for the detinned scrap, especially as it consists of the richest and purest iron available, because the consumption of sulphate of iron does not go hand in hand with the quantity of detinned scrap produced."

I inquired of the "Chemische Fabrik Uetikon" (vormals Gebrüder Schnorf), and they informed me that the detinning of tin scrap as described above was practiced at their plant in Uetikon from 1873 to 1893. Low prices of tin and the decreasing tin content of the scrap rendered the process commercially impractical; 300 to 400 tons of tin scrap were detinned per year. The process was not a continuous one, every cylinder worked independently.   C. OFFERHAUS.

Anaconda, Mont.

A New Iron-Carbon Phase, Osmondite.

By Henry M. Howe,

Professor of Metallurgy in Columbia University.

Heyn and Bauer[1], ever skillful and indefatigable, have discovered a new and important iron-carbon phase, osmondite, which appears to be a solid solution of carbon (or of an iron carbide) in normal or alpha iron. Austenite, be it remembered, is such a solution in allotropic gamma iron. There is a certain fitness in linking together the memories of these illustrious and dear friends, Roberts-Austen and Osmond, by the names of these two substances so closely related by allotropy, the very subject which interested them in common so greatly, and, indeed, led to their friendship, if I mistake not.
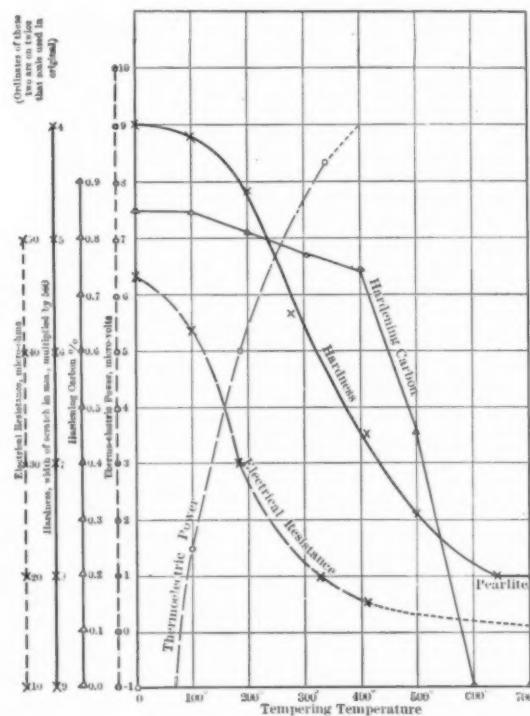

FIG. I.—IN THE TEMPERING OF STEEL, THE CHANGES IN THE PHYSICAL PROPERTIES PRECEDE THE CHANGE IN CARBON CONDITION. (HEYN & BAUER AND BARUS & STROUHAL.)

(The dotted parts of the curves for electrical resistance and thermo-electric power are interpolated or extrapolated.)

This discovery by Heyn and Bauer was made in the course of their study of the nature and progress of the changes which occur in the tempering of hardened steel of 0.95 per cent of carbon, and therefore approximately eutectoid. Their procedure was first to harden a series of like pieces of this steel by quenching them from 900° C. in cold water; next to mitigate or "temper" the effects of this hardening by reheating these pieces severally to a series of temperatures ranging from 100° to 600°; and finally to determine their physical properties, their microstructure, and the condition of their carbon.

I have prepared Fig. I so as to show simultaneously certain of their results, together with some of the probably comparable data of Barus and Strouhal which they recall.

That tempering changes the physical properties of hardened steel very greatly, and that it also changes the condition of the carbon from "hardening" or dissolved carbon, to "cement" carbon combined with iron as the definite iron carbide called "cementite," Fe_3C, has long been known. The important discovery now made is that the change in these physical properties precedes the change in the condition of carbon. Osmond[2] had indicated that as steel cools through the critical range, the change in physical properties precedes the change in carbon condition; and I had proved this fully;[3] but the conditions in this present investigation enable us to draw much firmer conclusions than were warranted by the earlier results of Osmond and myself.

Fig. I shows that, by the time that the tempering temperature has reached 400°, 70 per cent of the loss of hardness, 93 per cent of the loss of electric resistance, and nearly 100 per cent of the gain of thermo-electric power have taken place, whereas at most only 13 per cent of the change of the carbon from the dissolved or hardening to or towards the cementite state has occurred. In heating further to 600°, at least 87 per cent of the change of the carbon to the cementite state takes place. But this great change in carbon condition is accompanied by only 30 per cent of the loss of hardness, 7 per cent of the loss of electric resistance, and hardly any of the gain in thermo-electric power.

We should note that the whole argument rests, not on a certainty, but on what is only a reasonable probability. It rests on the reported condition of the carbon in these specimens, and this report in turn is based on the reasonable assumption that all of the carbon which escapes in the gaseous form when the steel is dissolved in 10 per cent sulphuric acid, with the air excluded, has been present in that steel as hardening carbon.

These results are in rough agreement with those of Dr. H. C. Boynton,[4] who found that nearly the whole of the hardness was removed in tempering before reaching 500°, a temperature at which, according to Heyn and Bauer, only about half of the carbon has changed from hardening to cement. This then is a further indication that the loss of hardness outruns the change in carbon condition. Though these two sets of results agree in this essential matter, there are some considerable discrepancies between them. Thus the loss of hardness on reaching 400° was 70 per cent of the total according to Heyn and Bauer, but only 26 per cent according to Boynton; and the temperature of rapid softening was from 200° to 300° according to the former, but between 450° and 500° according to the latter. These differences may readily be due to differences in the methods of determining hardness and in the composition of the steels treated. Nevertheless, it is to be hoped that Dr. Boynton may find it practicable to determine the carbon condition in his specimens, so as to establish more firmly the fact that the loss of hardness outruns the change from hardening to cement carbon.

In order to understand this matter clearly we should look back a little. Above the critical range (A_1 to A_3) the metal consists of a solid solution of carbon (or of an iron carbide) in the red-hot iron, and to this solid solution the name of "austenite" has been given. (See Fig. 2.) In case of the particular steel treated by Heyn and Bauer, this austenite is of the variety called "hardenite," i. e., it is of the eutectoid composition—about 0.95 per cent of carbon; and on this account it naturally undergoes only a single transformation in cooling through the critical range, viz.: the transformation called $Ar_{3, 2, 1}$, at or about 670° (S, Fig. 2). This transformation is

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[1] Uber den inneren Aufbau gehärteten und angelassenen Werkzeugstahls, von Direktor Professor E. Heyn und Diplom-Ingenieur O. Bauer. Mitteilungen aus dem Königlichen Materialprüfungsamt Gross-Lichterfelde West, 1906. See also Stahl und Eisen, 1906, XXVI., pp. 778, 915 and 991, and a most illuminating discussion by Osmond, to which I am much indebted; "Les Expériences du Prof. Heyn sur la Trempe et le Revenu des Aciers," Rev. de Metallurgie, III., Nov., 1906, pp. 621-632.

[2] Transformations du Fer et du Carbone, etc., pp. 38 and 87, 1888.

[3] The Hardening of Steel, Journal Iron and Steel Inst., 1895, II., pp. 293 et seq.

[4] Hardness of the Constituents of Iron and Steel, H. C. Boynton, Journ. Iron and Steel Inst., 1906, II., pp. 315-317.

from the solid solution or austenite state to the state of pearlite, which is a mechanical mixture of alternate sheets of pure iron or ferrite and of the definite iron carbide, cementite, Fe_3C. If the metal is suddenly cooled while it is passing through this transformation, its condition after cooling is found to vary according to the degree to which that transformation had taken place at the instant when the sudden cooling began; so that sudden cooling seems to preserve more or less accurately the condition which exists at the moment when the transformation is thus interrupted. In this way we have found that the metal passes through successive well marked stages, to which the names martensite, troostite, and sorbite have been given; and to these osmondite is now added. These stages might represent definite phases; or, shading off imperceptibly into each other, they might be only extremely fine mechanical mixtures of such phases. Table I. gives these successive stages and their conjectured constitution:

TABLE I.—THE STAGES OF THE TRANSFORMATION FROM AUSTENITE INTO PEARLITE.

Name.	Constitution.
Austenite	Solid solution of an iron carbide (hardening carbon) in gamma iron.
Martensite, a transition substance.	The same, with some of the gamma iron changed to beta and to alpha iron. Its most valuable property, its great hardness, is probably due to its beta iron.
Troostite, a transition substance.	The same, the quantity of gamma and beta iron constantly decreasing, that of alpha iron constantly increasing.
Osmondite	Solid solution of iron carbide (hardening carbon) in alpha iron.
Sorbite, a transition substance.	A mixture of a constantly decreasing quantity of osmondite with a constantly increasing quantity of pearlite, too fine to be resolved by the microscope.
Pearlite	A conglomerate or mechanical mixture of free alpha iron (alpha ferrite) with the iron carbide, Fe_3C, cementite.

Note to Table I.—Thus there appear to be three definite stages, the end ones, austenite and pearlite, and the midway stage, osmondite; and three intermediate indefinite stages of varying composition, martensite, troostite, and sorbite.

The austenite here referred to is "typical austenite," i. e., the austenite as it exists in the hot steel above A_3. It is never found in its typical or pure state in the cold, because, even under the most favorable circumstances, viz.: when a very high-carbon steel is cooled extremely rapidly from well above A_3, some of the gamma iron always changes into beta, and even into alpha iron, as is shown by the strong magnetic properties of this steel. The cold austenite, therefore, is really intermediate in composition between typical austenite and martensite, in spite of the fact that austenite and martensite in a given specimen of cold steel are often sharply distinguishable from one another. This simply means that, in such specimens, there are, side by side, microscopic regions in which the transformation from austenite towards pearlite has gone far, and others in which has only begun. The former are true martensite, the latter are justly called austenite, because in them the transformation has not yet gone far; quite as a felspar which has only just begun to degenerate into clay is still reasonably called felspar.

French writers, indeed, usually restrict the term "austenite" to that found in the cold steel, and call typical austenite, i. e., the solid solution as it exists above A_3, "gamma iron" (fer gamma).

The strongly marked needles so characteristic of cold martensite probably represent the structure of the true or typical austenite, from which it has sprung, because Saniter developed this same structure by etching steel when it was above A_3, and when it therefore by definition consisted of typical austenite. (Journ. Iron and Steel Inst., 1897, II., p. 128, Plate V., Figs. 2 and 3.) Thus a possible basis of definition of martensite might be "austenite, which is so slightly transformed as to show traces of acicular structure"; though this would lose sight of the most striking and valuable property of cold martensite, its extreme hardness, due probably to its large content of beta iron.

This present proof, that in tempering, very marked changes in the physical properties precede the change in the condition of carbon, has certain very important consequences. In the first place it indicates that the allotropic change in iron, which has been known since the remote historic day when Gilbert discovered that red-hot iron was not magnetic, is in itself the chief cause of the hardness of hardened steel; because this change in the properties of the steel which precedes the change in carbon condition can hardly be due to anything other than this sufficient cause. this known allotropic change in the iron itself. M. Osmond's earlier results and mine did not prove this, because the change in the properties of our non-eutectoid steel might have been due to the gradual separation of ferrite from the austenite which is known to occur before the change in carbon condition; whereas in the eutectoid steel of Heyn and Bauer there should be no such separation of ferrite from the austenite before the change in carbon condition.

In the second place, it puts before us the fact that, during the interval between the change of the iron from the allotropic to
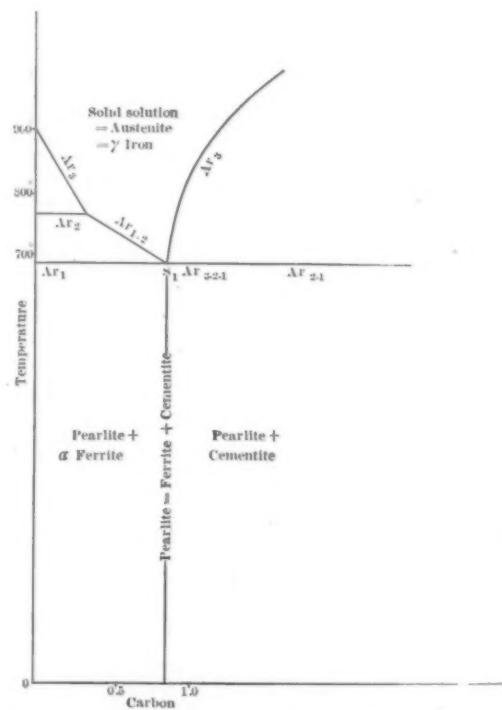
FIG. 2.—PART OF ROBERTS-AUSTEN OR IRON CARBON DIAGRAM.

the normal or alpha state, and that of the carbon from the hardening or dissolved to the cementite or carbide state, that carbon must be dissolved in that alpha iron.[8] Here, then, we are brought face to face with a new entity, a new phase, carbon dissolved in alpha iron. What shall it be called? Differing as it does from austenite in having its iron in the alpha instead of in the gamma state, it might have been called alpha austenite. But its discoverers have exercised their undoubted right to give it a proper name, calling it osmondite; and in this they have done wisely in my opinion.

What are the physical properties of this osmondite? From the conditions of its existence we can hardly expect ever to isolate it in the pure state, if indeed ever to identify it posi-

[8]"Carbon itself, that is to say free or elemental carbon, seems to be nearly insoluble in alpha iron. (See Journal Iron and Steel Inst., 1906, IV., p. 543, foot note.) Therefore, the dissolved carbon of the osmondite is likely to be, not elemental or free carbon, but an iron carbide, and if this is true of the carbon of the osmondite, it is probably true of that of the austenite whence the osmondite is derived. Here, then, we have an additional reason for regarding austenite as a solution, not of free carbon, but of an iron carbide, in gamma iron.

tively under the microscope, because it will always be mixed with the products of its own decomposition. But if its properties are well marked, we may hope to detect them in one way or another. For instance, if we take a series of tempered pieces, each tempered at a slightly higher temperature than the preceding, we find. first, that the rapidity of dissolving in dilute sulphuric acid, and, second, the intensity of coloration caused by etching with alcoholic hydrochloric acid, reach a maximum in the specimen tempered at 400°, and decrease as the tempering temperature departs from 400° either upwards or downwards. Are these two properties, which reach their maximum about simultaneously with the osmondite, properties of that osmondite? Let us consider. As that substance comes into existence, so simultaneously does a certain quantity of the carbon slip from the dissolved or hardening into the cementite state; because these transformations do not follow each other in single file like a line of soldiers, but overlap, so that while certain molecules are slipping from the martensite into the osmondite stage, certain others are simultaneously slipping from the osmondite through the sorbite into the pearlite stage. Now, the first particles of cementite thus born are sure to be much more finely divided than the mass of cementite later on, when, with further rise of temperature and the accompanying greater freedom of motion. its particles coalesce into larger masses. For instance, Heyn and Bauer find, beside the hardening carbon which escapes as gas when the metal is dissolved in extremely dilute sulphuric acid. and the cementite which is found as such in the residue from that dissolving, some additional carbon in that same residue. This may indeed represent the dissolved or solid-solution carbon of the osmondite, or a part of that carbon; but, on the other hand, as Osmond justly points out, it may represent simply the carbon of some cementite so finely divided that it is decomposed even by this weak sulphuric acid, with precipitation of its carbon in the residue.

Thus it may well be that this maximum rapidity of dissolving in sulphuric acid, and this maximum depth of coloring on etching in alcoholic hydrochloric acid, which characterize steel tempered at 400°, are due, not to the presence of osmondite, but to the finely divided condition of the almost nascent cementite or to some other special state of aggregation. Nevertheless, we have here a strong suggestion that these properties do belong to the osmondite, and a hint to future investigators to seek a definite answer to the question whether they do or do not.

But there are two properties of osmondite, its electric resistance and its hardness, as to which we may form firmer opinions, as I will now show.

From the fact that the increase of electric resistance caused by hardening is removed almost wholly by the time that the very richly osmonditiferous stage is reached, viz.: by the time that the tempering temperature reaches 400°. it is extremely probable that the electric resistance of osmondite is not much greater than that of pearlite.

That osmondite is much softer than martensite is, indeed, but one face of the reasoning which leads us to postulate the very existence of osmondite. We say that the loss of 70 per cent of the hardness in the 400°-tempered specimen is too great to be explained by the transfer of only 13 per cent of the carbon from the dissolved or hardening to the cementite state; that it implies the existence of a phase which is soft in spite of having its carbon in the dissolved state; and this soft phase we call osmondite. But beyond this we cannot go. We cannot say whether the still very considerable excess of hardness in the osmonditiferous 400°-tempered specimen over the hardness of pearlite is due to the greater hardness of osmondite than of pearlite, or to the martensite still remaining. In short, while osmondite is thus softer than martensite, we cannot tell how its hardness compares with that of pearlite.

The inequiaxing of osmondite remains to be studied. By inequiaxing I refer to the distortion or deformation of the crystalline grains of the metal, which normally are equiaxed. And right here let us consider the four means by which the sudden cooling of the hardening process may affect the properties of the metal. These are:

(1) Retaining the carbon in the hardening condition, labile below A_1.

(2) Preserving the iron in either or both of the allotropic states, beta and gamma, both labile below the critical range.

(3) Setting up permanent stress.

(4) Inequiaxing or distorting (ecrouissant) the crystalline grains, through differences in the contraction of different layers, due in part to differences in their rates of cooling and consequent contraction (æoliotachic contraction, i. e., different in rate even if equal in quantity), and in part to the different degrees to which the above transformations (1) and (2) and their consequent changes of volume (contraction differing in quantity) take place in the different layers.

There is a nearly general agreement that the second of the above four causes is the chief agency in the hardening of steel; but so talented an investigator as M. A. Le Chatelier assigns very great importance to the fourth, while the first cause seems to me to contribute powerfully, from the fact because it is only in the presence of much carbon that we ever get such extreme mineralogical hardness as that of hardened high carbon steel.

To this inequiaxing, M. Osmond calls attention. In order to understand the matter we should remember that the strengthening, embrittling, and hardening effects of processes like wire-drawing and cold rolling on the malleable metals and alloys in general are probably due chiefly to the distortion or inequiaxing which these processes cause, and that the removal of these effects which annealing causes is probably due to its re-equiaxing the metal, restoring it to its initial state. Prof. Heyn[a] has lately thrown invaluable light on this question, by showing that, in the annealing of hard-drawn wire, the equiaxing begins at 400° and completes itself when 600° is reached; and that simultaneously with this equiaxing the chief part of the weakening and toughening effects of the annealing take place.

From this fact that the inequiaxing of wire-drawn steel persists in chief part until the tempering temperature passes beyond 400°, it is extremely probable that the inequiaxing which hardening causes also persists in chief part up to this same 400°, so that not only the austenite, martensite, and troostite of hardened steel, but also the troostite and osmondite of tempered steel, are inequiaxed.[b]

M. Osmond lays great stress on this, and would base on it an estimate of the degree to which the effects of hardening by sudden cooling are due to inequiaxing as distinguished from the retention of allotropic iron and hardening carbon. He seems to attribute the properties of osmondite chiefly to its inequiaxing, and only in small part to its containing hardening carbon. But it seems to me that we do not know enough about its properties to be justified in doing more than speculate very tentatively about their cause. It is true that the fact that the electric resistance of the osmonditiferous 400°-tempered specimen is but slightly greater than that of pearlite, agrees well with the fact that the inequiaxing of wire drawing affects the electric resistance only slightly, and is wholly consistent with the belief that the properties of osmondite are due to its inequiaxedness. But the very vagueness of our knowledge of how hard osmondite is prevents our forming any strong opinion as to the source of its hardness. If we should later discover how hard osmondite really is, and if we should then find that its hardness exceeds that of pearlite to a degree which

[a] Uber die Nutzanwendung der Metallographie. Stahl und Eisen, 1906, XXVI., pp. 580-597.

[b] Needless to say, this inequiaxing is true neither of austenite as it exists in the redhot steel above the critical range, before sudden cooling begins, nor of these other stages, martensite, etc., as they are successively entered during slow cooling, if, indeed, they then are entered, instead of being skipped over.

corresponds roughly to the mild hardening which wire draw-
ing and other forms of inequiaxing cause, then we should be
inclined to attribute that hardness to the inequiaxing of the
osmondite.   But if we should find that the hardness of
osmondite exceeds that of pearlite to a much greater degree,
then we should incline to refer much of its hardness to its
containing hardening carbon.

Invoking the inequiaxing or distortion incidental to the hard-
ening of steel by sudden cooling to explain its marvellous
effects has always seemed to me to lack cogency; first, because
the most pronounced effect of this sudden cooling is the aston-
ishing increase in mineralogical hardness, a property on which
distortion as we know it in wire drawing has relatively little
effect; and, second, because if distortion were the true cause or
an important cause, then sudden cooling ought to cause like
effects at least in certain other alloys. But if there is any other
alloy in which it causes effects at all comparable with the hard-
ening of steel, I do not know it.

Rapid and Accurate Gas Analysis.

By Edwin Barnhart,

Chemist, By-Product Coke Plant, Maryland Steel Co.

Owing to the number of analyses of gases required daily and
the amount of time consumed an apparatus giving rapid and
accurate results was very desirable.
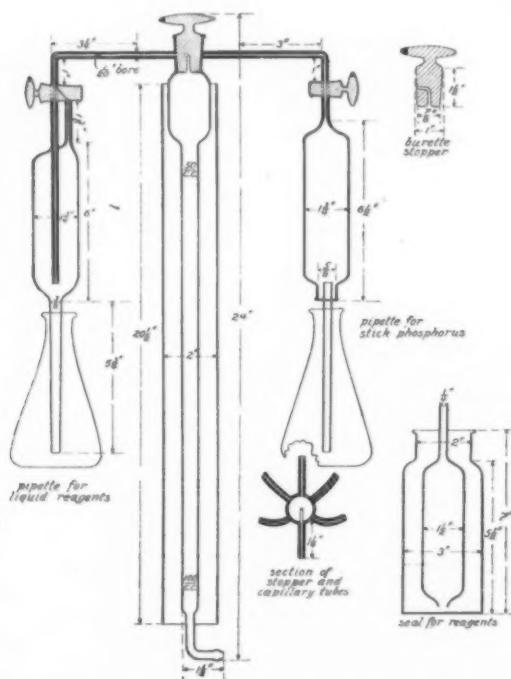
FIG. I.—SECTION OF ALL-GLASS PARTS OF APPARATUS.

Formerly the following two well-known types of apparatus
were used:

The Orsat-Muncke apparatus was used for the analysis of
blast furnace, producer and flue gases, while for the illuminat-
ing and fuel gases from coke ovens the latest modification of
the Hempel apparatus was used, a higher degree of accuracy
being essential in this work.

Those familiar with the Hempel apparatus will agree that
skillful manipulation is necessary; also the consumption of a
greater amount of time is required than with other types of
apparatus, while the Orsat apparatus, requiring less skill and
time for manipulation, has a limited application.

The apparatus described in this article is designed for the
classes of work before mentioned, and gives a high degree of
accuracy while requiring a minimum amount of time.

This special apparatus, as designed by N. M. Randall and
the writer, was made by Eimer & Amend, New York, about
two years ago, and has been in constant use here since. It has
given entire satisfaction and filled every requirement.

The time required for a complete analysis of coal or pro-
ducer gas with this apparatus is about 20 minutes, and under
favorable conditions this time has been reduced to 15 minutes.
This is a performance worthy of special note.

Numerous requests
having been made for
a description of this
apparatus. I have pre-
pared this brief arti-
cle, believing that the
apparatus represents
an improvement in the
method of gas analy-
sis worth recording.

Fig. 1 shows the
section of all the
glass parts of the ap-
paratus. Fig. 2 shows
the mahogany sup-
port and mounting
for the apparatus.
Fig. 3 is a front view
with the explosion
pipette detached. Fig.
4 is a front view with
the explosion pipette
attached. Fig. 5 is a
rear view of the ap-
paratus, showing the
device for sealing the
reagents from the at-
mosphere. Fig. 6 is a
view of the top of
the burette, showing
the pipette connected.

The measuring bur-
ette is of 100 c. c.
capacity, the narrow
part of which is
graduated from 102 c.
c. at the bottom to 50
c. c. just below the
wide part, and is sub-

FIG. 2.—SECTION OF SUPPORT FOR
APPARATUS.

divided into 1/10 c. c. or 1/20 c. c. The burette has a white
back with a blue strip, to facilitate accurate reading. The
bottom of the burette terminates with a narrow tube for a
rubber connection with a leveling bottle. Between the burette
and the leveling bottle is a stop-cock, to facilitate manipula-
tion. The upper end of the burette terminates in a bottle-
neck fashion, which forms the casing for a plug or stopper.

On the outer circumference of this casing are six capillary
tubes 1½ inches in length, which communicate with the
burette when the stopper is in the proper position. By
this feature six, or a less number, of absorption pipettes
may be directly connected with the burette, thus eliminating
the long header capillary of the Orsat apparatus, which gives
rise to an error in measurement after absorption. This feature
also eliminates changing of pipettes during the process of
analysis, as is necessary with the Hempel apparatus.

In the event of an accumulation of dirt or grease in the
burette the stopper may be removed and the burette swabbed
out without disconnecting any part of the apparatus.

The stopper in the top of the burette revolves easily, fits
perfectly and has never caused the slightest inconvenience.

FIG. 3.—FRONT VIEW WITH THE EXPLOSION PIPETTE
DETACHED.

FIG. 5.—REAR VIEW, SHOWING DEVICE FOR SEALING THE
REAGENTS FROM ATMOSPHERE.

FIG. 4.—FRONT VIEW WITH THE EXPLOSION PIPETTE
ATTACHED.
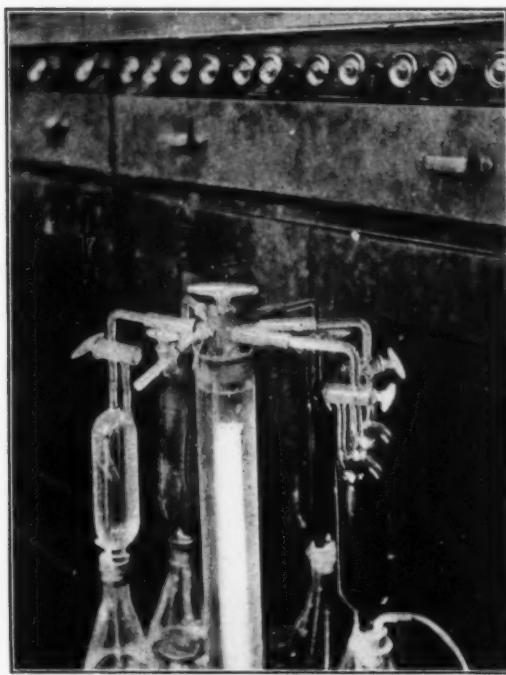
FIG. 6.—TOP OF BURETTE, SHOWING THE PIPETTE
CONNECTED.

The pipettes for liquid reagents shown in Fig. 1 have numerous advantages. The gas being caused to pass through the reagents is most rapidly absorbed. The pipettes are duplicates, and may be interchanged if necessary. The pipette proper terminates with a narrow tube, which is neatly fitted into an 8-ounce Erlenmeyer flask by means of a doubly per-

forated stopper, the flask making a support for the pipette, and acting as a reservoir for the reagent. The renewal of the reagent is accomplished by simply removing the flask and refilling, the capacity of the flask exceeding that of the pipette.

Stick phosphorus being a very good absorbent for small quantities of oxygen, the pipette shown on the drawing is used

for that purpose, the pipette proper being covered with block linen to protect the phosphorus from the light.

The reagents are protected from the atmosphere by the device shown on the drawing, which consists of a wide-necked bottle, which admits a tube drawn to a small opening at both ends, the upper end terminating with a narrow tube which passes through a doubly perforated rubber stopper in the bottle and connects with the flask containing the reagent by means of a rubber tube. The capacity of this tube is about 150 c. c., when the proper amount of water is placed in the bottle (about 125 c. c.) the sealing of the reagent requires no more attention.

For the determination of methane and hydrogen the Hempel mercury pipette is used.

The apparatus is supported upon a neat and substantial mahogany frame, which is shown in Fig. 2, of which the lowest diagram is a plan, while the middle diagram shows the section at line A-B, and the upper diagram represents a neat mahogany bench, which is placed in front of the apparatus to support the mercury pipette when attached; it is also used when gas samples are taken into the apparatus from a collecting tube or bottle.

The base of the wooden frame is 18 inches square, in the center of which is a cylindrical block 6 inches high and 3 inches in diameter; upon this block the burette and jacket are supported; 10 inches above the base and fastened to it by five 1-inch rounds is the support for the pipettes and flasks. This also keeps the burette and jacket in an upright and rigid position. The apparatus thus mounted may be moved very conveniently. The part of the frame upon which the Erlenmeyer flasks rest is covered with a thin sheet of black paranite.

Supposing the sample under examination to be coal gas, the method of precedure would be as follows:

100 c. c. of gas is admitted to the measuring burette through capillary in front, the reading immediately taken and the gas passed into the first pipette on the left containing sodium hydrate. The second pipette contains sodium hyrogallol, the third bromine water, the fourth ammoniacal cuprous chloride, and the fifth to remove the ammonia and the last traces of carbon monoxide contains an acid solution of cuprous chloride. After the volume of carbon monoxide has been noted the residual gas is confined over the acid solution.

88 c. c. of air is now admitted to the burette, 12 c. c. of the residual gas mixed with it, and mixture exploded over mercury in the Hempel pipette; the contraction noted and the carbon dioxide formed absorbed with sodium hydrate.

The following two analyses show a comparison of work done with this apparatus with that done with Hempel's apparatus, No. 1 being made with the Hempel:

	No. 1.	No. 2.
Carbon dioxide	2.05%	2.10%
Oxygen	.10	.05
"Illuminants"	4.30	4.25
Carbon monoxide	6.90	7.00
Methane	36.50	36.71
Hydrogen	44.25	44.27
Nitrogen	5.90	5.62

Analysis No. 2 required 20 minutes for completion.

The following analyses are the work of two men, a portion of the same gas and the same apparatus being used by each:

	No. 1.	No. 2.
Carbon dioxide	2.80%	2.80%
Oxygen	.60	.60
"Illuminants"	2.60	2.40
Carbon monoxide	6.80	6.80
Methane	32.14	30.90
Hydrogen	45.14	46.20
Nitrogen	9.92	10.30

Both of the above analyses required 16 minutes for completion.

Metallurgical Calculations.

By J. W. Richards, Ph. D.
Professor of Metallurgy in Lehigh University.

"Bringing Forward" of Copper Matte.

The above term is the old Welsh expression for the further treatment of mattes which gradually eliminates iron and sulphur and finally results in "crude" or "blister" copper, usually 90 to 99 per cent pure. The matte obtained by the first smelting operation varies considerably in richness, between 20 and 50, or even up to 60, per cent of copper. The reason it is not always made high in copper is that the richer the matte the more copper goes into the slag; one of the expert metallurgist's best accomplishments in copper smelting is to make a rich matte and poor slag. The making of slag of the best composition, and the use of extra large settlers or fore-hearths, helps most to this end. Having then this "first matte" the problem of the metallurgist is to get from it the metallic copper which it contains.

The Welsh Process.

The principle employed is to partially roast the matte and then to smelt it down to a richer matte and a ferruginous slag. The grade of matte formed in this smelting depends entirely upon the amount of roasting to which the matte has been subjected, the more sulphur eliminated by roasting the less can be present to form matte and the richer the matte.

Illustration: A matte containing 21.36 per cent of copper and 22.95 per cent of sulphur is roasted until its sulphur contents is two-thirds eliminated. What grade of matte can be expected on the subsequent smelting?

The sulphur left is $22.95 \div 3 = 7.65$. The 21.36 of copper requires 5.34 of sulphur to form Cu_2S, leaving $7.65 - 5.34 = 2.31$ of sulphur to form FeS. This forms $2.31 \times 88/32 = 6.35$ FeS. The resulting matte cannot contain more FeS than this; its composition will therefore be approximately:

Copper	21.36 = 64 per cent.
Iron	4.04 = 12 "
Sulphur	7.65 = 23 "

	33.05

In practical work a richer matte than this will be formed in reverberatory furnace smelting and a slightly poorer matte by shaft furnace smelting, because in the former there is some reaction between the oxides and sulphides of the roasted ore, resulting in an expulsion of SO_2 during smelting, and in the latter, using carbonaceous fuel, the temperature is so high and reducing action so strong that metallic iron is formed and enters the matte, practically acting as if the matte contained some Fe_2S, and thus diluting the matte.

This roasting is a slow operation unless the matte is crushed and roasted fine. Lump matte is very little pervious to gases; it roasts slowly. By breaking a lump in half we, on an average, increase its surface 50 per cent, and therefore the exposed surface available for oxidation increases, for a given weight of material, very quickly as its size is decreased. For auto-roasting by its own self-generated heat of oxidation the finer the better, and roasting thus in lump form is impracticable because of the slowness of the operation.

Pyritic smelting of matte is probably altogether out of question as far as pure pyritic smelting without carbonaceous fuel is concerned. Using some coke, however, an oxidizing smelting analagous to partial pyritic smelting is possible, as was proved by Mr. Freeland, at Isabella, Tenn. Such a concentrating pyritic smelting is more feasible with a low-grade matte than with a high grade, because there is more iron and sulphur to oxidize. It will be profitable to calculate closely the details of this matte smelting to rich matte, and to compare it with the details of the smelting of raw ore in the same furnace—the subject of Problem 107 (July issue).

Problem 109.

W. H. Freeland, at Isabella, Tenn. (see *Engineering and Mining Journal*, May 2. 1903), smelted a low-grade matte without preliminary roasting in a water-jacketed Herreshoff furnace, having a free area at the tuyeres of 21.7 square feet. The analyses of materials used and the products are as follows:

Charges.

	Matte.	Raw Ore.	Laboratory Samplings.	Slags.	Quartz.	Coke.
Cu	20.00	2.79	2.45	0.73	.....	.....
Fe	47.15	43.26	31.07	39.20	1.45	2.30
S	24.00	29.18	14.84	1.75	0.32	1.58
SiO²	0.44	10.01	22.66	30.90	96.79	8.41
CaO	0.10	6.32	5.71	8.51	0.23	.....
MgO	.....	1.39	2.03	2.71	.....	.....
Zn	2.05	2.56	2.05	2.88	.....	0.00
Al²O³	0.82	1.00	1.15	1.90	0.32	3.56
Mn	0.53	0.69	0.75	0.85	.....	0.00
O	4.91	.....	3.39	11.37	0.38	1.00
C	.....	.....	13.90	.....	.....	83.86
CO², etc..	.....	2.80	.....	.....	.....	.....
Loss	.....	.....	.....	.....	0.39	.....

Products.

	Matte.	Flue Dust.	Slags.
Cu	49.63	2.49	0.60
Fe	25.24	24.79	43.99
S	23.00	8.91	1.19
SiO²	0.26	31.43	33.72
CaO	.....	3.31	2.03
MgO	.....	1.18	0.57
Zn	1.53	3.81	2.12
Al²O³	.....	3.93	2.16
Mn	0.39	0.30	0.50
O	.....	3.97	12.86
C	.....	15.88	.....

The charges and products per 24 hours and per 1,000 of matte used were:

Charges:

Matte	47.5 tons	1,000 lbs.
Raw ore	8.1 "	170 "
Laboratory samplings	1.6 "	34 "
Slag	7.6 "	160 "
Quartz	15.7 "	330 "
Coke	4.5 "	95 "

Products:

Matte	19.1 tons	401.6 lbs.
Flue dust	0.6 "	12.0 "
Slag	56.1 "	1182.2 "

Blast applied, 4,500 cubic feet displacement, at 17 ounces pressure. Assume temperature of gases 450° C., and that they contain no CO, SO² or free O² (no analyses are given). Assume matte and slag issuing from the furnace at 1,300° C. (no temperature is given).

Required:

(1) A balance sheet of everything entering and leaving the furnace.

(2) The volume efficiency of the blowing plant.

(3) The heat generated per minute per square foot of cross-section in the focus of the furnace.

(4) The theoretical temperature at the focus.

(5) The proportion of the heat generated in the focus by the combustion of carbon and by the oxidation of sulphides.

(6) The concentration effected in this smelting.

(1) **Balance Sheet** (*per 1,000 of matte smelted*).

Charges.		Matte.	Flue Dust.	Slag.	Gases.
Matte (1,000)					
Cu	200.00	199.31	0.30	0.39	.....
Fe	471.50	101.36	2.97	367.17	.....
S	240.00	92.18	.....	.....	147.82
SiO²	4.40	1.04	.....	3.36	.....
CaO	1.00	1.00	.....	1.00	.....
Zn	20.50	6.14	.....	14.36	.....
Al²O³	8.20	.....	.....	8.20	.....
Mn	5.30	1.57	.....	3.73	.....
O	49.10	.....	.....	49.10	.....
Ore (170)					
Cu	4.74	.....	.....	4.74	.....
Fe	73.54	.....	.....	73.54	.....
S	49.60	.....	1.07	14.15	34.38
SiO²	17.02	.....	3.77	13.25	.....
CaO	10.74	.....	0.40	10.34	.....
MgO	2.36	.....	0.14	2.22	.....
Zn	4.35	.....	0.46	3.89	.....
Al²O³	1.70	.....	0.47	1.23	.....
Mn	1.17	.....	0.04	1.13	.....
O	2.40	.....	.....	2.40	.....
CO²	2.38	.....	.....	.....	2.38
Samplings (34)					
Cu	0.83	.....	.....	0.83	.....
Fe	10.56	.....	.....	10.56	.....
S	5.05	.....	.....	.....	5.05
SiO²	7.70	.....	.....	7.70	.....
CaO	1.94	.....	.....	1.94	.....
MgO	0.69	.....	.....	0.69	.....
Zn	0.70	.....	.....	0.70	.....
Al²O³	0.39	.....	.....	0.39	.....
Mn	0.26	.....	.....	0.26	.....
O	1.15	.....	0.48	0.67	.....
C	4.73	.....	1.91	.....	2.82
Slags (160)					
Cu	1.17	.....	.....	1.17	.....
Fe	62.72	.....	.....	62.72	.....
S	2.80	.....	.....	.....	2.80
SiO²	49.44	.....	.....	49.44	.....
CaO	13.62	.....	.....	13.62	.....
MgO	4.34	.....	.....	4.34	.....
Zn	4.61	.....	.....	4.61	.....
Al²O³	3.04	.....	.....	3.04	.....
Mn	1.36	.....	.....	1.36	.....
O	16.90	.....	.....	16.90	.....
Quartz (330)					
Fe	4.78	.....	.....	4.78	.....
S	1.06	.....	.....	.....	1.06
SiO²	319.41	.....	.....	319.41	.....
CaO	0.76	.....	.....	0.76	.....
Al²O³	1.06	.....	.....	1.06	.....
H²O	2.93	.....	.....	.....	2.93
Coke (95)					
Fe	2.19	.....	.....	2.19	.....
S	1.50	.....	.....	.....	1.50
SiO²	7.99	.....	.....	7.99	.....
Al²O³	3.38	.....	.....	3.38	.....
C	79.67	.....	.....	.....	79.67
H²O	0.27	.....	.....	.....	0.27
Blast (2,065)					
O²	476.63	.....	.....	81.24	395.39
N²	1588.77	.....	.....	.....	1588.77
	3854	401.60	12.01	1176.05	2264.84

Notes on the Balance Sheet.

The sulphur and carbon of the charge passing into the gases are, from the balance sheet, 192.61 and 82.49; respectively. We can assume all the carbon in the gases as CO² and all the sulphur as SO² except, say, half of that from the ore. This

leaves 192.61 − 17.19 = 175.42 of sulphur to be oxidized at the focus:

Oxygen for sulphur $= 175.42 \times \dfrac{32}{32} = 175.42$

Oxygen for carbon $= 82.49 \times \dfrac{32}{12} = 219.97$

Total to burn sulphur and carbon at focus   395.39

Oxygen for Fe in slag $= 499.31 \times \dfrac{16}{56} = 142.66$

Oxygen for Mn in slag $= 6.48 \times \dfrac{16}{55} = 1.88$

Oxygen for Zn in slag $= 23.56 \times \dfrac{16}{65} = 5.77$

Total in slag   150.31

Total oxygen in gas and slag $= 545.70$
Oxygen furnished by solid charges   69.07

Oxygen furnished by the blast   476.63
Nitrogen furnished by the blast   1588.77

(2) The furnace receives 2,065 pounds of blast per 1,000 of matte concentrated. This represents at 0°:

$$\frac{2065 \times 16}{1.293} = 25{,}550 \text{ cubic feet.}$$

Per 2000 lbs. matte =	51,100	" "	
Per 47.5 tons matte =	2,427,250	" " "	per day.
=	101,135	" " "	hour.
=	1,686	" " "	minute.
At 50° C. =	1,958	" " " "	
Blower displacement =	4,500	" " " "	

Efficiency of blower $= \dfrac{1,958}{4,500} = 0.435 = $ **43.5** per cent.   (2)

(3) To calculate the heat generated at the focus we will assume that all the fixed carbon of the coke is there burned to CO², and that the rest of the oxygen blown in produces the reaction characteristic of pure pyritic smelting. There is treated per minute:

$$\frac{47.5 \times 2000}{1440} = 66 \text{ lbs. of matte,}$$

and the carbon burned per 1000 of matte is 82.49 lbs., generating
82.49 × 8100 = 668,169 lb. Calories,
and absorbing 219.97 lbs. of oxygen. This leaves 476.63 − 219.97 = 256.66 lbs. of oxygen to oxidize sulphides.

Since by the "pyritic smelting" reaction, 2O² generates 161,560 calories, there is generated per pound of oxygen thus used
161,560 ÷ 64 = 2,524 lb. Calories,
and per 1000 lbs. of matte smelted we have
2,524 × 256.66 = 677,820 lb. Calories,
but heat generated by carbon = 668,170 " "

Total = 1,345,990 " "

Since this is per 1000 lbs. of matte smelted, we have, per minute
1,345,990 ÷ 1,000 × 66 = 88,835 lb. Calories,
and per square foot of smelting zone area, per minute
88,835 ÷ 21.7 = **4,094** lb. Calories.   (3)

Comparing this with the 732,930-pound Cal. generated at the focus in smelting 1,000 pounds of ore, and the 3,575-pound Cal. there generated per square foot per minute, we see that the matte smelting requires more heat per unit of charge, princi-

pally because the smelting is done more slowly. Radiation losses are over twice as great per unit of charge treated when concentrating matte than when ore concentrating. This points to the utility of hard driving when smelting matte, as the direction likely to yield greatest economy.

(4) Taking as a basis of calculation 1,000 pounds of matte treated, there is generated at the focus 1,345,900-pound Cal., there is used 2065 pounds of blast, and there arrives at the focus all of the charges except the flue dust, CO² and H²O of charges, and approximately one-half of the sulphur contained in the raw ore. We therefore have arriving at the focus approximately:

82.5 lbs. of fixed carbon.
1133.0 lbs. of sulphides.
545.0 lbs. of inert slag-forming material.

These come to the focus preheated by the ascending gases, and assuming them to be preheated to 1,000°, we can find the correction to be used for their sensible heat:

Carbon	82.5 × 380 =	31,350 lb. Calories.
Sulphides, melted	1133.0 × 200 =	226,000 " "
Slag-forming material	545.0 × 174 =	94,850 " "
		352,200 " "
Heat generated at the Focus		1,346,000

Total in the hot products, at Focus 1,698,200 " "

Letting t be the theoretical temperature at the focus, then we have:

Heat in Slag $\quad 1176[300 + (t - 1100)0.27]$
" " Matte $\quad 402[200 + (t - 1000)0.14]$
" " S vapor $\quad 17[179 + (t - 445)0.11]$
" " SO² $\quad \dfrac{351}{2.88}[0.36t + 0.0003t^2]$
" " CO² $\quad \dfrac{302}{1.96}[0.37t + 0.00022t^2]$
" " N² $\quad \dfrac{1589}{1.26}[0.303t + 0.000027t^2]$

The calorific capacity of these products at t° is therefore
$$29{,}858 + 858.7t + 0.1046t^2$$
and making this equal to the heat available at the focus, we have
$$0.1046t^2 + 858.7t + 29{,}858 = 1{,}698{,}200$$
whence $\qquad t = $ **1622°**.   (4

This is 53° higher than we calculated for the same furnace smelting ore, with only one-third as much coke. If the coke were omitted from this charge the theoretical temperature would be:

$$t = \mathbf{1388°}.$$

Such a theoretical temperature at the focus would not suffice to form slag, supply radiation and conduction losses, and see the matte and slag safely out of the furnace, except with very hard driving and very fast running in a large furnace.

(5) The heat generated by oxidation at the focus has already been calculated. The proportion to credit to carbon is

$$\frac{668{,}170}{1{,}345{,}990} = 0.496 = \mathbf{49.6} \text{ per cent.}$$

and to oxidation of sulphides   **50.4**   "   (5)

In the ore smelting these figures were found to be 31 and 69 per cent, respectively.

(6) The ratio of concentration is usually found by comparing the per cent of copper in the material treated with that in the material produced. This would give in this case:

$$\frac{49.63}{20.00} = \mathbf{2.48}$$ (6)

A more reasonable factor, however, is the ratio of weight of

fresh copper-bearing materials treated to weight of copper-bearing materials produced which must be further treated. This would be in this case:

$$\frac{1204}{414} = 2.9$$

whereas in the ore smelting it was

$$\frac{1080}{148} = 7.3$$

"BLISTER-ROASTING" OR ROASTING-SMELTING.

When a matte has been concentrated to somewhere between 70 and 80 per cent of copper it is called "white metal," and is in shape for reduction to metallic copper:

	Cu^2S.	FeS.
With 70 per cent copper, matte contains	87.5	12.5
With 80 per cent copper, matte contains	100.0	0.0

The problem being to get metallic copper, the operation is entirely one of oxidation; first, slow melting down of the lumps of matte in a highly oxidizing atmosphere on the hearth of a reverberatory furnace; second, continued oxidation until all the sulphur is removed and the bath remains as metallic copper, saturated with Cu^2O and Cu^2S.

During the melting down the matte is oxidized superficially to such an extent that when fusion is finally complete the copper oxides have reacted upon the iron sulphides sufficiently to eliminate all the iron from the matte. The reactions and phenomena of this period are exactly those of the matte concentration processes.

After the melting down sulphur continues to be oxidized with formation of copper oxide, and then this latter reacts with more of the sulphide to set free metallic copper.

(a) $\qquad 2Cu^2S + 3O^2 = 2Cu^2O + 2SO^2$.

(b) $\qquad Cu^2S + 2Cu^2O = 6Cu + SO^2$.

(c) $\qquad Cu^2S + O^2 = Cu + SO^2$.

Reactions (a) and (b) are probably consecutive, but assuming them simultaneous we have equation (c).

Thermochemically, equation (a) analyses as follows:

$2(Cu^2, S)$ = $2(20,300)$	=	40,600 Calories	*absorbed.*
$2(Cu^2, O)$ = $2(43,800)$	=	87,600 "	*evolved.*
$2(S, O^2)$ = $2(69,260)$	=	138,520 "	"

Algebraic sum	= 185,520 "	"
Per kilo. of Cu^2S	= 583 "	

Similarly, equation (b):

(Cu^2, S)	=	40,600 Calories	*absorbed.*
$2(Cu^2, O)$ = $2(43,800)$	=	87,600 "	"
(S, O^2)	=	138,520 "	*evolved.*

Algebraic sum =	10,320 "	"
Per kilo. of Cu^2S =	65 "	"

Equation (c) gives:

(Cu^2, S)	=	40,600 Calories	*absorbed.*
(S, O^2)	=	138,520 "	*evolved.*

Algebraic sum =	97,920 "	"
Per kilo. of Cu^2S =	615 "	"
Per kilo. of copper liberated =	770 "	"

The net result of these figures is to show that the first reaction evolves a large amount of heat, that the second is thermally about neutral, and that the two together constitute a highly exo-thermic reaction. When we reflect that a kilogram of melted Cu^2S only carries some 250 Calories, and a kilogram of melted copper not over 200 at any furnace temperature, the large excess of heat above calculated shows up very strikingly.

In a reverberatory furnace the rate of oxidation is so slow that but minor advantage is taken of the heat of oxidation of the Cu^2S.

Illustration: In a reverberatory furnace, 8 tons of "white metal" is smelted to blister copper in 48 hours, using 5 tons of coal. About what proportion does the heat of oxidation of the charge bear to the heat of combustion of the coal?

Assuming the tons to be 1,000 kilos., the white metal to be nearly pure Cu^2S, and the calorific power of the coal 6,000, we have:

Heat of oxidation of the bath	8000 × 615	= 4,920,000	Calories.
" of combustion of coal	5000 × 6000	= 30,000,000	"
" requirement for 48 hours		34,920,000	"
" requirement per hour		727,500	"

Proportion of heat requirement furnished by oxidation of both:

$$\frac{4,920,000}{34,920,000} = 0.141 = 14.1 \text{ per cent.}$$

The above figures teach us, however, that when the charge is once melted, that if the oxidation of the bath could be performed quickly enough it alone would keep the furnace up to heat. For example, the furnace requires an average of 727,500 Cal. per hour to keep it up to heat. The heat of oxidation would therefore supply this for

$$\frac{4,920,000}{727,500} = 6\frac{3}{4} \text{ hours,}$$

which means that if the bath, when melted, could be oxidized in that time all exterior firing would be unnecessary after the charge had been once melted. Some companies force air onto the surface of the bath, and one company blows compressed air through wrought iron pipes into the bath, producing the required oxidation in one-fifth the time usually required, and saving greatly in coal.

Bessemerizing Copper Matte.

John Hollway, in 1878, patented the process of oxidizing matte to metallic copper in an apparatus similar to the Bessemer steel converter; in 1880, Manhès, in France, was successful in accomplishing this result, and in 1884 ran the first commercial plant at the Parrot works in Butte. While the principles are similar the details are very different from the blowing of pig iron to steel.

In oxidizing pig iron the carbon, silicon, manganese, etc., which are to be oxidized out rarely exceed 10 per cent, while the iron itself is oxidizable, and some 3 to 20 per cent may be lost. In oxidizing matte some 40 to 70 per cent of the whole charge is to be oxidized, a very voluminous slag results, and the operation lasts five to fifteen times as long. Towards the end of a "steel" blow, the pure iron formed is itself oxidizable, and is not chilled but really heated by the passing of the blast through it; in a "matte" blow the pure copper separating at the end is not oxidizable under the prevailing conditions, and therefore is only chilled by the blast if the latter strikes it. On the latter account, tuyeres in the bottom are impracticable when Bessemerizing matte, since they become filled with chilled copper; it is imperative to use lateral tuyeres which, by the swinging of the converter, are kept always below the surface of the matte but above the pool of copper as it separates out and sinks to the bottom.

The two best treatises for details of bessemerizing copper matte are Jannettaz "Les Convertisseurs pour le Cuivre" and Dr. F. Mayr's "Das Bessemern von Kupfersteinen"; very satisfactory information can be found in Dr. Peter's "Modern Copper Smelting" and "Principles of Copper Smelting," in Hixon's "Notes on Lead and Copper Smelting and Copper Converting," and in Schnabel's "Handbook of Metallurgy," last edition. Vol. I.

Assume that a converter is just emptied, is at a bright red heat (1,100°), and that a charge of melted matte at, say, 1,100°

(setting point 1,000°), is poured into it. The lining is some 60 c. m. thick, the outside shell of the converter is at about 200° C., and the surface is losing heat at a nearly steady rate of, say, 50 Cal. per square meter of outside surface per minute (10-pound Cal. per square foot). A converter of 25 square meters outside surface would thus lose 1,250 Cal. per minute if standing still. If it had 3,000 kg. of liquid matte in it, with a specific heat of 0.14, the latter would give out 3,000 × 0.14 = 420 Calories for every degree which it cooled, and would therefore cool off about 1,250 ÷ 420 = 3° per minute. If poured in 100° above its setting point it might be some 30 minutes in cooling to its setting point and 70 minutes in setting, assuming no radiation losses through the throat, i. e., that the throat were tightly covered.

Under such conditions, if blast is turned on, the reaction is

$$2FeS + 3O^2 + 2SiO^2(\text{lining}) = 2(FeO, SiO^2) + 2SO^2$$

and the heat evolved is

Decomposition of	2FeS	= 2(24,000)	= −	48,000	Calories.
Formation of	2FeO	= 2(65,700)	= +	131,400	"
Union of 2FeO with	2SiO²	= 2(8,900)	= +	17,800	"
Formation of	2SO²	= 2(69,260)	= +	138,520	"

	Total	= +	238,720	"
Heat evolution per 1 kg. FeS	=		1,356	"
Heat evolution per 1 kg. O²	=		2,487	"

Theoretical Temperature Rise.

Supposing we oxidize an amount of FeS equal to 1 per cent of the weight of matte. Let us calculate the theoretical rise in temperature of the contents of the converter.

The oxygen required is 3O² to 2FeS, or per kilo. of FeS.

Oxygen required	= 96 ÷ 176 = 0.545 kg.
N² accompanying	= 1.818 "

Air required	= 2.363 "
Volume = 2.363 ÷ 1.293	= 1.827 m³.

In being raised from say 50° C. to 1100°, the assumed temperature of the matte, the air will absorb

$$1.827[0.303 + 0.000027(1150)] \times 1050 = 641 \text{ Calories.}$$

This leaves available, for raising the temperature of the products of the reaction:

$$1,356 - 641 = 715 \text{ Calories.}$$

The immediate products are:

99.	kg.	of unoxidized matte.
1.50	"	" liquid slag.
0.73	"	" SO² gas.
1.82	"	" N² gas.

The heat capacities of these, at 1100°, is as follows, per 1° C.:

Matte	99 × 0.14 = 13.86	Calories.
Slag	1.50 × 0.27 = 0.41	"
SO²	0.73 ÷ 2.88 × 1.02 = 0.25	"
N²	1.818 ÷ 1.26 × 0.36 = 0.52	"

	Sum = 15.04	"

Theoretical temperature rise

$$715 \div 15.04 = \mathbf{47.5° C.}$$

The above rise represents the *rate* at which the temperature tends to rise at the beginning of the blow. Supposing this amount of FeS (1 per cent) is oxidized in 1 minute, the temperature at the end of 1 minute would rise 47.5° less the cooling off in 1 minute, which latter might be from 2° to 10°, according to the size of the converter and its charge, thickness of lining, etc. For practical purposes the cooling-off rate may be assumed as nearly constant, but the heating-up rate is very variable. As the FeS disappears the amount of slag increases, while that of the matte decreases; but since 1.50 kilos. of slag with a calorific capacity of 0.41 Cal. per degree takes the place of 1 kilo. of matte with a calorific capacity of 0.14 Cal. per 1°, the heat capacity of the products is increasing 0.27 Cal. for each 1 per cent of FeS oxidized, while the available heat for raising temperature is slightly decreasing, because of the higher

temperature of the bath and therefore the greater chilling effect of the air. Assuming that the bath cools 5° during the time that 1 per cent of FeS is being oxidized out, we can calculate the following table:

FeS Oxidized.	Temp. at Start.	Heat Absorbed by Air.	Net Heat Available.	Calorific Capacity of Products.	Temp. Rise.
0 to 1%	1100°	641	715	15.04	42.5°
1 " 2%	1142.5°	670	686	15.31	40°
2 " 3%	1182°	694	662	15.58	37°
3 " 4%	1219°	722	634	15.85	35°
4 " 5%	1254°	742	614	16.12	33°
5 " 6%	1287°	768	588	16.39	31°
6 " 7%	1318°	789	567	16.66	29°
7 " 8%	1347°	809	547	16.93	27°
8 " 9%	1374°	823	533	17.20	26°
9 " 10%	1405°	847	509	17.47	24°
At 10%	1429°	...	...	.....	....

There is no object in extending above table, because it is constructed on the particular assumption that radiation losses would amount to 5° during the burning out of 1 per cent of FeS. This quantity would evidently vary with the size of the converter, the amount of matte being treated and the speed of blowing, because as the contents become hotter their rate of cooling would be increased. The object of the above table, so far as it went, was to show that 47.5° was the theoretical rise for the first 1 per cent, but that the theoretical rises for succeeding percents would be less and less; in such manner, instead of rising (47.5 − 5) × 10 = 425° for an oxidation of 10 per cent of FeS the actual rise figures out only 329°.

One of the most necessary data which is badly needed for these converters, and in fact for Bessemer converters in general, is the heat loss by radiation and conduction, in other words, how much heat would be lost by the charge if simply standing still, how much would the temperature of a given charge fall per minute if standing still? This could be easily obtained by running in a charge of pretty hot matte, and following its temperature curve as it cools, without any necessity of letting it freeze, but merely starting up the blast when the rate of cooling had been satisfactorily determined. If these determinations were coupled with details as to the temperature of the outside air, its velocity of impingement against the converter, the temperature of the outside shell, the area of radiating surface and the thickness of the lining, we would soon get data with which to render entirely definite and exact the whole thermal investigation of a "Bessemerizing" operation. This should be supplemented by analyses of the gases during the blow and the temperature curve of the contents as the blow progresses. Scientific metallurgists must, at present, simply assume many of these data, because of lack of them. We are looking to the metallurgical directors of copper plants for some of this badly-needed technical data.

Problem 110.

W. Randolph Van Liew (*Trans. Am. Inst. Mining Eng.*, 1904, p. 418) gives the following analyses of a charge of matte blown to blister copper in a Bessemer converter:

	Cu.	Fe.	S.	Zn.
Matte	49.72	23.31	21.28	1.19
10 minutes	50.20	23.15	20.95	1.20
20 "	56.88	17.85	19.74	0.84
30 "	64.60	10.50	18.83	0.70
40 " (last slag skimmed)	76.37	2.40	16.30	0.45
70 " (blister copper).	99.120	0.038	0.159	0.09
	As.	Sb.	Ag.	Au.
Matte	0.11	0.14	0.152	0.00055
10 minutes	0.09	0.12	0.147	0.00048
20 "	0.08	0.10	0.176	0.00069
30 "	0.08	0.13	0.191	0.00083
40 " (last slag skimmed)	0.08	0.13	0.240	0.00110
70 " (blister copper).	0.0012	0.006	0.312	0.00111

The percentage composition does not exhibit clearly the relative time and amount of the elimination of impurities, because of the varying weight of the bath.

Required:

(1) Assuming 1,000 kilograms of matte to be treated, find the weight at each period of the blow of the matte.

(2) The loss of each constituent of the bath during each period.

(3) The heat evolution during each period.

(4) The loss of heat per minute due to radiation and conduction, assuming that the heat starts with matte at 1.100° and ends with blister copper at 1.200°, and that 1 per cent of copper (reckoned on the matte) is oxidized during the last period.

(1) The first question is to find some constituent of the matte, whose weight does not vary during the blow, to serve as a basis for the calculations. If the analyses be taken as reliable in all details (we can make no other assumption) we see that there is very little loss of anything in the first 10 minutes, evidently because of the low temperature of the matte. Afterwards, iron falls off rapidly, also sulphur and zinc, while silver and gold increase in percentage, because of the falling off in weight of the bath as a whole. The slag, up to the last skimming, contains usually but very little copper; in the last period we are told to assume a loss of 10 kilos. of copper by oxidation. The most rational basis for calculating the weight of the bath is to assume the copper contents constant for the first 40 minutes.

Copper in 1000 kg. of matte at starting	497.2 kg.

Weight of matte at starting					1000.0 "
"	"	"	10 minutes	= 497.2 ÷ 0.5020 =	990.4 "
"	"	"	20 "	= 497.2 ÷ 0.5688 =	874.1 "
"	"	"	30 "	= 497.2 ÷ 0.6460 =	769.7 "
"	"	"	40 "	= 497.2 ÷ 0.7637 =	651.0 "
"	" metal	70 "		= 487.2 ÷ 0.9912 =	491.5 " (1)

From the analyses given, and calling the shortage of percentage in the analyses oxygen, we have the following table of weights and eliminations: (2)

Per 1000 kg. of Original Matte.

	Cu.	Fe.	S.	O.
Start........	497.2	233.1	212.8	41.0
Eliminated...	0.0	3.8	5.3	0.1
End 10'.....	497.2	229.3	207.5	40.9
Eliminated...	0.0	73.3	35.0	2.9
End 20'.....	497.2	156.0	172.5	38.0
Eliminated...	0.0	75.2	27.6	−0.3
End 30'.....	497.2	80.8	144.9	38.3
Eliminated...	0.0	65.2	38.8	12.0
End 40'.....	497.2	15.6	106.1	26.3
Eliminated...	10.0	15.4	105.3	24.9
End 70'.....	487.2	0.2	0.8	1.4

Zn.	As.	Sb.	Ag.	Au.	
11.9	1.1	1.4	1.52	0.0055 =	1000.0
0.0	0.2	0.2	0.06	0.0007 =	9.6
11.9	0.9	1.2	1.46	0.0048 =	990.4
4.6	0.2	0.3	−0.08	−0.0012 =	116.3
7.3	0.7	0.9	1.54	0.0060 =	874.1
1.9	0.1	−0.1	0.07	−0.0004 =	104.4
5.4	0.6	1.0	1.47	0.0064 =	769.7
2.5	0.1	0.2	−0.09	−0.0008 =	118.7
2.9	0.5	0.8	1.56	0.0072 =	651.0
2.5	0.5	0.8	0.03	0.0017 =	159.5
0.4	0.0	0.0	1.53	0.0055 =	491.5

Our table is not absolutely accurate, as can be seen from an apparent gain in both silver and gold in the periods 10' — 20'

and 30' — 40'. This is caused by a loss of copper during those periods, but the amounts of gold and silver are too small to serve as a base for revising the table. If we were to assume the gold as constant it would make a smaller weight of bath at the ends of those periods, but the figures are not reliable enough to make this correction worth while.

The very small total loss in the first 10 minutes and the loss of time thus occasioned could in all probability be obviated by putting the matte hotter into the converter at the start.

A graphic representation of the course of a blow is usually made by plotting the *percentages* of each element in the bath at given periods. *This plan is largely misleading;* the diagram should be made by plotting the calculated *weights* of each element present at the given periods, such as are found in the above table.

(3) The heat evolution is to be found by taking the weights of each element oxidized out, calculating the heat of its oxidation and formation of slag, and subtracting the heat necessary to break up the equivalent amount of its sulphide. The heat necessary to separate the sulphides from each other is unknown.

Period I.—Start to 10'.

Heat of oxidation

				Cal.	Cal.
Fe	to FeO.SiO²	3.8 × 1332	=	5,062	
S	" SO²	5.3 × 2164	=	11,469	
As	" As²O³	0.2 × 1043	=	209	
Sb	" Sb²O²	0.2 × 695	=	139	
					16,879

Decomposition of sulphides.

Fe from FeS	3.8 × 429	=	1630	
As " As²S³	0.2 × 2000 (?)	=	400	
Sb " Sb²S³	0.2 × 1433	=	287	
				2,317

Net heat evolution   14,562

The other periods are similarly calculated, and yield the following results:

	Start–10'	10'–20'	20'–30'	30'–40'	40'–70'	⅓ last.
Heat of oxidation..	16,879	179,797	162,476	174,316	257,046	85,682
Decomp. of sulphides	2,317	35,321	33,719	30,113	10,410	3,470
Net heat evolution	14,562	144,476	128,757	144,203	246,636	82,212

The last column is added for comparison, being the heat evolution per average 10' in the last period. (3)

(4) The loss of heat by radiation and conduction can be found, as a whole, by assuming the converter body to contain the same heat at finishing as at starting, which is a likely assumption, since the lining loses somewhat in weight but ends up at a higher temperature. Then we know how much heat was in the original matte at 1,100°, how much was generated, how much is in the slag and copper, and can calculate approximately how much is carried out in the gases. These enable us to find, by difference, the loss by radiation and conduction which can then be averaged up per minute.

			Calories.
Heat in 1000 of matte at 1100°		=	214,000
Net heat generated in the blow		=	678,635
Total available		=	892,635
Heat in 491.5 Copper, at 1200°		=	85,995
" " 424.0 SO², " 1000°		=	97,020
" " 947. N², " 1000°		=	248,160
" " 550. Slag, " 1250°		=	187,000
Heat accounted for			618,175
Loss by radiation and conduction		=	274,460
Loss per minute, per 1000 kg. matte		=	**3,920** (4)

It is thought that the principles explained and the methods of calculation illustrated will suffice to show to copper metal-

lurgists how important information is obtainable by applying the principles of thermo-chemistry to copper smelting, and to indicate the lines along which experiment and results of measurement and observation are greatly to be desired.

[The next instalment of these calculations will be concerned with the electrometallurgy of copper.]

Electrothermic Combustion of Atmospheric Nitrogen.

A very interesting paper on the fixation of atmospheric nitrogen was recently presented before the Manchester Section of the Society of Chemical Industry by Mr. F. Howles, who was one of the earliest workers in the field, and made in 1898-9, together with Mr. McDougall, a valuable investigation of the principles of the combination between oxygen and nitrogen in air under the influence of electric discharges.

Mr. Howles agrees with the theory now generally accepted that the oxidation of nitrogen in the arc is a purely thermal phenomenon. With increasing temperature part of the oxygen and nitrogen in the air will combine, and for every temperature when equilibrium is reached there is a definite volume of concentration of the oxide in the gas mixture which has been determined by Nernst. The higher the temperature the higher the concentration of nitric oxide.

The ordinary high-tension arc in air consists of three superimposed zones, all mounting upwards and of different size and temperature. Zone 1, the lowest zone, carries the major portion of the current, and therefore has the highest temperature, about 4,200° C. It is probable that in this zone alone the oxidation of nitrogen takes place. Zone 2, or the middle zone, is greenish-blue in color with a temperature of at least 1,400° C. Zone 3, or the highest zone, forms the greatest bulk of the flame. It is of a pale yellowish-brown color, and its temperature is 900° to 100°, according to Muthmann and Hofer, though Mr. Howles thinks this figure is too low.

While in zone 1 the nitric oxide is formed, the reverse happens in zones 2 and 3. When the gas mixture containing the nitric oxide is removed from the zone 1, and passes through zones 2 and 3, the nitric oxide is dissociated and part of the useful work performed in zone 1 is undone.

The first condition of getting a high yield is to get as high a temperature of the arc as possible in zone 1. The second is to remove the gas mixture from the sphere of influence of the arc as quickly as possible after the reaction has taken place in order to prevent the dissociation in the cooler parts of the arc. Quite intimately connected with this second condition is Mr. Howles' third condition, namely, the necessity of reducing by some means the relative values of zones 2 and 3 of the flame, in which dissociation of nitric oxide takes place, and at the same time to increase the capacity of the first zone in which the nitric oxide is produced.

A fourth important consideration in the technical production of nitric oxide is the concentration of large amounts of energy in a unit of plant. With the ordinary high-tension flame it is not possible or at least not advisable to use currents of more than 0.1 to 0.2 amp.; for as the researches of Mr. McDougall and Howles have shown, a diminished yield of nitric oxide results. But as the yield of oxide is a function of the energy consumed, since the reaction $N_2 + O_2 = 2NO$ requires an expenditure of 43,200 cals., a plant constructed for the utilization of a large number of low-current arcs would entail the erection of an enormous number of units, if any large quantity of acid had to be produced. The up-keep and labor charges on such a plant would necessarily be high, and to this fact is attributable the failure of the earlier processes.

Mr. Howles gave a brief review of various technical processes which have been proposed or used for the fixation of atmospheric nitrogen. "The process proposed by Mr. McDougall, which yielded about 300 kilos. of nitric acid per kilowatt-year is now only of historic interest, as is also that of Bradley and Lovejoy, since both processes suffer from the inherent defects mentioned above."

Mr. Howles then refers to the process of J. de Kowalski and M. Moscicki, which was described and illustrated in our Vol. II., p. 152. He comments on this process as follows: Whether a current of high periodicity and voltage, such as the one used by them, possesses some special advantage or whether the increased yield is merely the result of some mechanical property of an arc so produced, does not appear to be clear from the experiments of these authors. The latter view is probable, since the yield of nitric acid obtained by Kowalski and Moscicki has been far surpassed by subsequent workers, who used currents of only moderate periodicity and voltage. This process also, if worked commercially, would require a large number of units of plant, since only 2½ kilowatts are condensed in each arc.

Mr. Howles then passes over to the discussion of the well-known process of Birkeland and Eyde, which has been described in detail and with illustrations repeatedly in our former volumes. Concerning prior work along the same lines the following notes are given: "Plücker (*Poggendorf's Annalen*, Vol. 133, p. 252), in 1861, had shown that when a high-tension discharge passed between electrodes, situated in a magnetic field and at right angles to the magnetic lines of force, a disc of sparks resulted, and that when the phenomenon occurred in a vessel filled with air, the formation of brown oxides of nitrogen was observed. Lehmann (*Die elektrischen Lichterscheinungen und Entladungen,* 1898, p. 353), in 1898, applied this arrangement to the high-tension electric flame, and obtained a similar spreading of the arc. When a direct current is used, the arc resembles a half circle; with an alternating current an approximately circular disc is formed."

After having described the industrial development of the Birkeland-Eyde process in Norway, Mr. Howles discusses some investigations of the Badische Anilin und Soda Fabrik. When using alternating currents for the production of the electric flame it is necessary to introduce, in series with the arc, an inductance, which effects a displacement of phase, thus regulating the current and enabling the flame to burn steadily. A transformer constitutes such an inductance, the iron cores of which, when the current is passing, are converted into magnets. In a patent taken out in 1904 (English patent 5,688), the Badische Anilin und Soda Fabrik claim the use of such a magnetic field for spreading out the arc. They thereby avoid the use of a separate current for exciting the magnets. Of this arrangement other advantages are also enumerated, notably the self-inductive action in the arc, which the cyclical motion imparted by the alternating current to the magnetic field produces, whereby the inner resistance, and consequently the stability of the arc, is increased.

This particular combination of apparatus, however, does not appear to have been technically applied, as in 1906 the same company make use of another method of producing arcs of great power (English patent 9,279, of 1906). The arrangement consists essentially of an iron tube, 1 meter or more in length, at one end of which an insulated electrode is situated, a single electrode electrically connected to the tube being inserted at the opposite end. On passing a current of some few thousand volts an arc is established between the insulated electrode and the wall of the iron tube adjacent to it. If, now, air, with a whirling motion be blown into the tube, the arc travels along the wall to the opposite electrode, and as long as the current of air is maintained the arc continues to burn steadily between the electrodes. Several insulated electrodes are also used, each in separate tubes, the latter, however, all leading into a common chamber, in which is situated the electrode electrically connected with the tube. It is, moreover, found that, by the use of either single-phase or polyphase currents, several arcs in one tube can be obtained burning quietly side by side and uniting at the upper end of the tube, which is

earthed so that no danger is incurred by touching it; 100 kilowatts of electrical energy have been employed in each arc. This apparatus is extremely simple, and should good yields of acid be obtained there appears to be no reason why the process should not be a commercial success.

Of other methods of burning atmospheric nitrogen it will be interesting to notice those of Naville and Guye (French patent 361,827 of 1905), and of Pauling (French patents 368,715 and 368,717 of 1906), who appears to be working in conjunction with the Salpetersäure Industrie Gesellschaft. The former workers, by rotating a disc-shaped electrode E—situated in a cylinder of refractory material C—over a metal tube A, conveying the air to be treated, and which forms the second electrode, obtained a spreading of the arc round the periphery of both the tube and the disc. By this method a yield of 400 kilos. of nitric acid per kilowatt-year has been obtained.

The apparatus devised by Pauling consists of either straight or curved fixed electrodes A E inclined to one another in a vertical plane. At regular intervals solid conductors C, which are fixed on the periphery of a revolving wheel W, pass between the lower ends of the electrodes, thus causing an arc to spring across. By means of an air blast, conveyed by pipes P, the arc, continually increasing in size, is made to travel upwards along the electrodes, until the points E are reached, when it becomes extinguished. As each solid conductor passes the electrodes a new arc is formed, which in its turn goes through the same process. In another method the wheel carrying the solid conductors is not used. Opposed tuyeres, conveying an air blast, cause the arcs, which are continually produced at A, to lengthen and break at E, as described in the previous process.

FIG. I.—APPARATUS OF NAVILLE AND GUYE.

Pauling has also endeavored to oxidize nitrogen without the intervention of electrical energy (English patent 21,828 of 1902). By passing a mixture of air and steam through thin-walled porcelain tubes heated to incandescense he observed the formation of nitric oxide and hydrogen. The latter gas diffused through the walls of the tubes, and this diffussion was increased, either by means of a pressure inside the tubes or a partial vacuum outside. Later, the gases issuing from the incandescent porcelain tubes were rapidly lowered in temperature by the injection of cold air (English patent 7,870 of 1906), thus minimizing the action due to the phenomenon of reversibility.

FIGS. 2 AND 3.—APPARATUS OF PAULING.

Häusser (English patent 12,401 of 1906) also avoids the use of the electric flame in the combustion of nitrogen. He reverts to the explosion method of oxidation, the feasibility of which was first demonstrated by Bunsen and Kolbe in 1846. The special apparatus used by Häusser consists of a gas engine, in which the usual mixture of air and gas is exploded. The products of combustion are, however, rapidly cooled by the injection of cold water into the combustion chamber. As with the process last described there appears to be no published data relating to the yield of acid thus obtained.

In discussing the results obtained, Mr. Howles states that the yield of 650 kg. of nitric acid per kilowatt-year represents the greatest output so far realized. Assuming a mean flame temperature of 3,200° C., this represents an efficiency of 79.3 per cent of that theoretically possible.

The relative reduction in volume of zones 2 and 3 of the flame, which is so essential to successful working, would appear to have been partially realized in the Birkeland-Eyde furnace. The spreading of the "current paths" by magnetic force should tend to equalize the temperature of the flame, and prevent that great opportunity for gradual temperature fall which is observed in the ordinary high-tension flame, and which is so inimical to the attainment of a satisfactory yield.

Against the advantage, however, must be placed the energy required to maintain the magnetic field, amounting as it does to 10 per cent of the quantity consumed in the arc and which is not included in calculating the yield of acid. The temperature of the flame might be raised by increasing the resistance of the gases, by working under pressures above that of the atmosphere.

It is interesting in this connection to note some experiments of Muthmann and Hofer (Berichte, Vol. XXXVI., 1903), who found that by increasing the pressure of the gases surrounding the arc from 1 to 1.4 atmospheres, the velocity of the air passing into the arc chamber could be accelerated, and although the exit gases contained the same percentage of nitric oxide, yet the yield was increased threefold per unit of energy consumed. Such a result could only be due to increased flame temperature, caused by the added resistance of the air to the passage of the current consequent upon increased pressure.

These experiments are important, containing, as they do, two elements of success, i. e., an increase in flame temperature and a more rapid removal of the nitric oxide from the arc, due to the greater air velocity, and this without increased dilution. An extension of this work would probably yield interesting results.

Against the increased yield, however, must be set the cost of compressing the gases and the difficulties which always obtain in practice in working at high temperatures under pressure.

Absorption of Nitric Oxide and the Preparation of Nitric Acid.

After leaving the furnace, the air contains about 2 per cent by volume of nitric oxide, which becomes rapidly converted, by means of the excess oxygen present, into nitrogen peroxide. The mixed gases then pass on to absorption towers, which present no special features of construction and down which water or dilute acid flows. In the case of the last tower, milk of lime is used, as it is difficult to absorb the last traces of NO_2 by means of water alone. By this process one obtains an acid of not more than 50 per cent strength.

The preparation of a concentrated nitrous-free acid from the nitrous gases constitute one of the most serious problems in connection with this process. The reaction represented by the equation:

$$2NO_2 + O + H_2O = 2HNO_3,$$

does not take place in the absorption towers, such an equilibrium appears to exist only in the gaseous state. On condensation the right-hand side of the equation is not produced. The most concentrated acid which has so far been obtained by the condensation of nitrous gases in water in the presence of oxygen corresponds to the formula $HNO_3, 2H_2O$, and possesses a density of 40.6° B., representing 63.63 per cent of anhydrous nitric acid. The formation of this acid takes place, according to the following equation, in the Lunge and Rohrmann plate towers:

$$2NO_2 + O + 5H_2O = 2(HNO_3, 2H_2O),$$

from which acid of 40° to 41° B. is obtained. By passing the gases, however, through towers down which water flows, an equimolecular mixture of nitric and nitrous acids results,
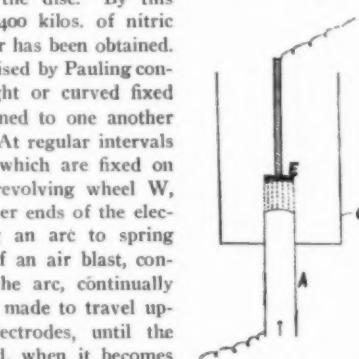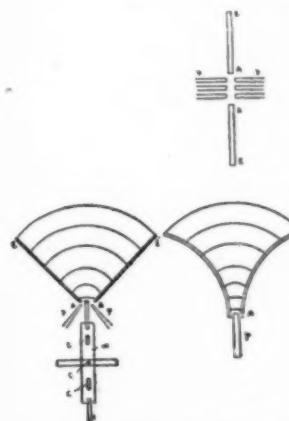
which, at the most, cannot attain a concentration greater than that obtained in the Lunge towers. Attempts at further concentration, by the passage of nitrogen peroxide through the solution, simply result in an increase of nitric acid at the expense of the nitrous. The strongest acid is thus never free from nitrous acid, and each succeeding absorption tower contains less and less nitric acid, whilst at the same time the nitrous acid increases, for as the free oxygen in the gases becomes consumed the NO and NO_2 tend to react as N_2O_3, yielding only nitrous acid. It is not possible to prepare much stronger acid by fractionating the 50 per cent acid from the first absorption tower, since a product of minimum vapor pressure, boiling at 120°, and containing 68 per cent of anhydrous acid, is obtained as residue.

Thus in order to prepare the most concentrated acid by the nitrogen combustion process it would be necessary to either add the 50 per cent acid to concentrated sulphuric acid until a dilution of say, 54° B., be obtained (54° B. = 120° Tw = 68.5 per cent of H_2SO_4), and distill off the nitric acid; or to prepare a salt of nitric acid, and distill in the usual way with sulphuric acid or a bisulphate.

An electrolytic method for concentrating and oxidizing the weak tower acid has lately been patented (French patent 368,716 of 1906). The process consists in refrigerating the oxides of nitrogen evolved during electrolysis at the cathode, and leading them in the liquid state slowly to the anode compartment of the cell, where in presence of the nascent oxygen there generated a solution of pure nitric acid results, all nitrous acid undergoing oxidation. It is not stated if this process has proved a commercial success.

Thus, although the electrochemical production of nitric acid has attained a fair degree of efficiency in some of the processes touched upon, the problem of directly manufacturing from the furnace gases a 98 per cent acid has not yet been solved.

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The Use of Producer Gas In the Chemical Industries.

By Oskar Nagel, Ph. D.

In Germany great progress has been made lately in the application of producer gas for melting, calcining, roasting, heating with reducing or oxidizing flame and evaporating. A large number of sulphate furnaces are now operating with producer gas and the total saving of labor and fuel in most of them amounts up to 50 per cent. The general advantages of producer firing are:
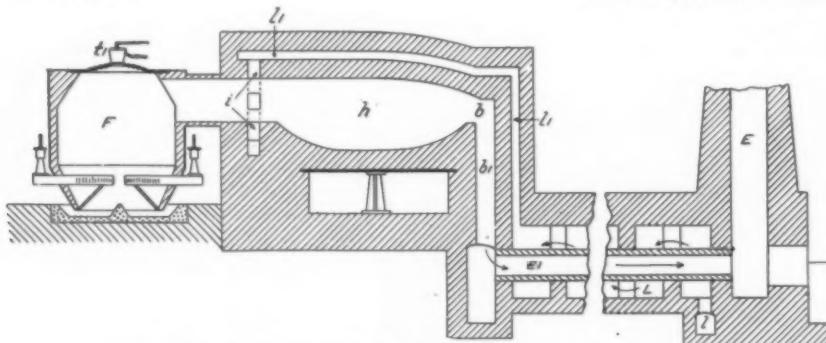
NO. 1.—REVERBERATORY FURNACE FIRED WITH PRODUCER GAS.

a. By regulating the quantity of gas and air conveyed to the place of combustion a perfect and uniform combustion is obtained.

b. According to requirements an oxidizing or reducing flame can be obtained, which is of importance to the chemical and metallurgical industries.

c. The process of combustion can be limited to a small place,

whereby the effect to be attained is frequently reached better and quicker than with direct firing.

d. It is possible in every case to utilize perfectly the waste heat by preheating the combustion air or the gas.

e. The material to be burned or worked does not come in
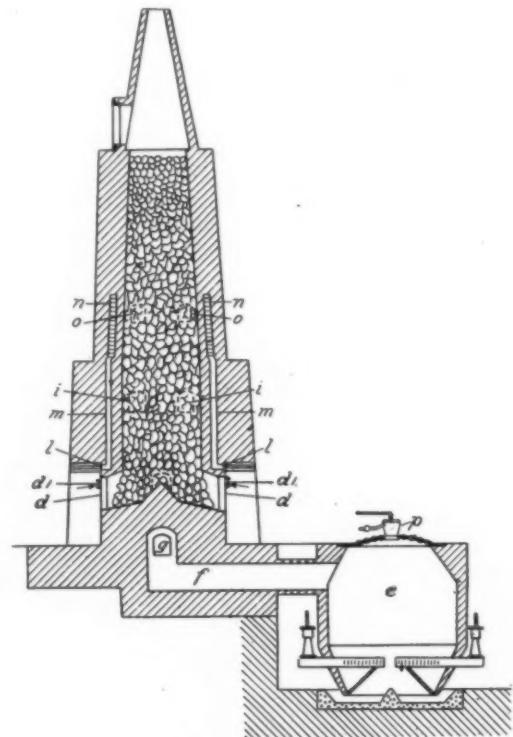
NO. 2.—LIME KILN FIRED WITH PRODUCER GAS.

contact with the solid fuel or ashes, which is of importance for the manufacture of lime and of clay products.

f. The attendance is easier, is simpler and cheaper than with direct firing.

g. The places of the gas production and gas consumption can be separated; thence one producer or a battery of producers can furnish fuel to a large number of furnaces. A long distance of producer and furnace is rather an advantage, as it causes the complete condensation of steam in the producer gas.

The special advantages of importance to sulphate works and other chemical factories are:

a. The possibility of burning low-grade fuel.

b. Production of a uniform product on account of the regulability of the temperature.

Producer Gas-Fired Reverberatory Furnace.

The principal outlines of a gas-fired reverberatory furnace are shown in Fig. 1. The change from direct fire to gas fire consists mainly in the addition of the gas producer and recuperator between furnace and chimney. The recuperator consists mainly of a system of fire-clay pipes (e l) which connect the flue b with the chimney F. This pipe system is built into a wider channel L in which the air required for the combustion of the producer gas is introduced at l. The air goes in chan-

nel L around the pipe system, as shown in the cut by arrows, absorbs the heat of the escaping fire gases and carries this heat back to the furnace through the channels and openings i. These channels are connected with the hot air chamber L of the recuperator by air slits or air channels l'. In these air slits which are arranged throughout the width of the furnace arch the air is brought to a still higher temperature. Thence at the fire bridge incandescent producer gas is mixed with incandescent air, causing a perfect combustion. In working with a reducing flame the combustion is nearly smokeless. It gets perfectly smokeless by the use of a slight excess of air. The saving is effected by the higher temperature obtained, by the recovery of the heat in the recuperator, by reducing the radiation of the fire-place, by the exact regulability of the firing, by the perfect combustion and by the longer life of the fire-brick.

LIME KILNS.

As lime is largely used in the chemical industries a description of a producer-fired gas lime kiln, as shown in Fig. 2, will be of interest.

The gas generated in the producer goes through sewer f to the gas distributing flue g, from which the gas passes through vertical channels to the gas inlet openings i. Being under pressure the gas is equally distributed over the entire area. The combustion air enters at d', absorbs the heat stored in the lower part of the shaft and is highly preheated while the burned material in the furnace is cooled at the same time. The air arrives (on account of the high temperature) at the place of combustion at a certain pressure, which prevents the drawing in of excess air and effects the uniform distribution of the air as well as of the gas. The combustion of the producer gas by the hot air is taking place between and above the gas inlets. That part of the producer gas which rises upward immediately at the inlet openings does not meet the amount of air necessary for combustion, which, however, is introduced above the gas inlet through the air inlets o. This "second" combustion air enters the shaft at l, rises through m, is distributed in the channels m n behind the fire-brick lining of the combustion zone proper and finally enters the shaft through openings o. By means of this arrangement the fire-brick lining is air cooled from the outside and the rising producer gas completely burned by the second combustion air.

It is evident that with such a producer-gas installation a uniform heat is obtained, that the utilization of the heat is far superior to direct fire, and that a great saving in the fuel consumption (25 to 50 per cent) is effected. Further advantages are the production of pure material and longer life of the shaft.

A producer especially adapted for this kind of work is the Herrick producer, which is manufactured by the Industrial Gas Co., of New York. It is shown in the cuts connected to a reverberatory furnace and lime kiln. It is of the water seal type, and the special construction of its tuyeres insures the uniform distribution of the blast, thereby effecting the formation of gas of constant composition.

The way of mixing the gas and the air is of fundamental importance for getting a complete and smokeless combustion. In a wide hearth the gas will advantageously be introduced in a number of parallel currents. In this case the air has to be applied analogously, so that there is one gas channel corresponding to every air channel. As the air is heavier than the gas, it is by no means immaterial whether the air channels are constructed above or below the gas channels. If the air is introduced above the gas a quicker combustion is obtained; reduction processes are conveniently performed with "upper" air. If the air is introduced below the gas a slower combustion i. e., a longer flame, is obtained; oxidation processes are conveniently performed with "lower" air. While parallel currents of gas and air are used if a large area is to be heated, the gas and air are brought together under an angle for heating a narrow space; for heating a small object gas and air are combined at a right angle.

The Fixation of Nitrogen.*

BY NORMAN WHITEHOUSE.

The object of this research was to obtain a workable commercial process by which the nitrogen of the atmosphere could be obtained combined as ammonia or nitrate, and was undertaken at the suggestion of Sir William Ramsay. It is obvious that if any commercial process is to be worked out using a metallic nitride as the nitrogen carrier, then one of the following methods of treatment must be possible:

1. The nitride chosen must be directly reducible with hydrogen, giving ammonia together with the metal, a lower nitride or a hydride.

2. A nitride when treated with steam will always give ammonia and the oxide of the metal; but if this reaction is used the oxide produced should be one which is conveniently reducible with hydrogen or carbon.

3. If the nitride will react with hydrogen sulphide or hydrogen chloride, this reaction may be employed, provided the sulphide or chloride is reducible.

The reasons for the failure to work out a commercial process on these lines may be summarized as follows:

1. With certain exceptions, such as cerium, metals which combine with atmospheric nitrogen were found not to be directly reducible with hydrogen.

2. The oxide of metals which will react with molecular nitrogen are also non-reducible with hydrogen or carbon at a reasonably low temperature, that is to say, under about $1,500°$ C., above which temperature the working becomes both difficult and costly.

3. In some cases hydrogen sulphide and hydrogen chloride do not react with the nitrides of those elements which combine directly with nitrogen. But when they do, the resulting compounds are not themselves easily reducible.

The first experiments were carried out with *magnesium* nitride, as it is common knowledge that magnesium, if strongly heated, combines with nitrogen giving this compound. As is well known, it reacts with water with violence, giving rise to ammonia and the hydroxide of the metal

$$Mg_3N_2 + 6HOH = 2NH_3 + 3Mg(OH)_2.$$

It also burns if strongly heated in air, forming oxide and free nitrogen. It was obvious that if any commercial process was to be worked out, using magnesium nitride as the nitrogen carrier, it would be necessary to prevent the magnesium changing to oxide in its cycle of reactions. With this in mind, some experiments were undertaken to find out if it were possible to effect the reduction of magnesium nitride directly with hydrogen at various temperatures between $400°$ C. and about $1,000°$ C. An iron tube was used to contain the porcelain boat holding the nitride, and the whole was heated in an electric tube furnace. After repeated experiments it was found that if the hydrogen were freed from every trace of oxygen by passing the gas over red-hot copper, and from moisture by bubbling it through sulphuric acid drying tubes, then no appreciable reduction took place. The difficulty experienced in these experiments of getting rid of every trace of air brought home the unsuitability of magnesium nitride for a commercial process; it was also evident that in any commercial undertaking "water gas" would have to be employed. Now, as hydrogen and carbon monoxide cannot be completely separated from one another by any cheap process, the gas would have to be used as a whole. This was found to be impossible, as the magnesium was oxidized, free carbon, cyanamide and other products being formed.

Attention was then turned to *titanium*, the affinity of which for oxygen is not so pronounced as that of magnesium, while that for nitrogen is at least equally great. Experiments were

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* A paper read before the London section of the Society of Chemical Industry, from the Journal of the Society, July 15.

made with two nitrides of this element, namely, titanic nitride, a bronze-brown powder (Ti_2N_4, according to Wöhler), and titanium dinitride, TiN_2, an amorphous blue powder. The dinitride was prepared by heating the dioxide in a current of ammonia gas at about 600° C. Titanic nitride is obtained when the metal is heated in nitrogen. It is also, and was, actually obtained for these experiments by the ignition of ammonia-titanium tetrachloride in a stream of ammonia gas.

$$3(TiCl_4 4NH_3) = Ti_2N_4 + 8NH_4Cl + 4HCl$$

Strong ammonia was added to a concentrated solution of commercial titanous chloride, and the resulting blue-black precipitate was dried and ignited in a current of air, when the dioxide was obtained as a yellowish-white powder. The average amount of titanium dioxide obtained was 51 grms. per pound of the concentrated solution of titanous chloride. The preparation of the ammonium titanium tetrachloride was a somewhat lengthy process. It consisted of heating the dioxide in a current of carbon tetrachloride at about 450° C. A mixture consisting mainly of titanium tetrachloride and carbon tetrachloride was obtained in the cooled receiver, and by fractional distillation the titanium tetrachloride of b. p. 136° C. was separated. Dry ammonia gas was passed into the titanium tetrachloride, and the solid canary-yellow double salt was obtained. As before mentioned, this, on ignition, gives titanic nitride.

An analysis was made as follows: 1.647 grms. of titanic nitride was weighed in a porcelain boat. The titanium oxide, estimated by igniting the nitride in air, weighed 1.927 grms., corresponding to 70.2 per cent of titanium in the nitride. As the nitride was prepared from commercial oxide an accurate analysis was impossible, but this percentage agrees fairly well with the 72.0 per cent of titanium in pure Ti_2N_4. A similar analysis was made with the dinitride. The percentage of titanium was found to be 64.2 per cent, as compared with 63.3 per cent required by the formula, TiN_2.

The direct reduction of these nitrides with hydrogen was attempted first in an iron tube, and afterwards in hard glass. The use of the iron tube was given up as, although the nitride in the boat did not lose weight, enough ammonia was formed to turn litmus paper blue, and even to be smelt. As this could only have come from the iron tube, it seemed probable that in passing the current of ammonia previously through the tube over the titanium dioxide to form the dinitride, some of the iron had become converted into iron nitride, which was subsequently reduced by hydrogen, giving ammonia. In hard Jena glass, and using a gas furnace, and up to the highest temperatures attainable with this combinaton, no reduction of either of the nitrides of titanium was observed.

As ammonia gas passed over the oxide at a red heat gave the dinitride, the possibility of being able to attain the same result by passing a mixture of nitrogen and hydrogen over the dioxide at a red or white heat suggested itself. This was tried at temperatures ranging from a low red heat to 1,500° C., using a silica tube, but no nitride was formed, the dioxide being simply reduced to black titanous oxide. As this experiment was not successful, and as hydrogen is more active as a reducing agent in the presence of finely divided nickel, another similar experiment was performed in which the titanium dioxide was mixed with an equal weight of nickel oxide, and the whole finely ground and then reduced with hydrogen at 350° C. A mixture of hydrogen and nitrogen was passed over it at this temperature, but no nitride was obtained, although a small trace of ammonia was present in the issuing gas.

An attempt was also made to produce a nitride of titanium by heating the sulphide in a mixture of hydrogen and nitrogen. The sulphide was obtained by heating titanium dioxide in a current of carbon bisulphide vapor to a red heat. 2.073 grms. of the sulphide ignited to dioxide gave 1.495 grms., equal to 43.2 per cent of titanium; this agrees approximately with the 42.8 per cent required for the formula TiS_2. During the attempt to produce the nitride by this method, hydrogen sulphide was evolved but no nitride obtained, only a lower titanium sulphide, the percentage composition of which agreed with the formula, Ti_2S_3. The experiment was conducted with 2.196 grms. of the sulphide, during which a loss of 0.284 grms. took place, which corresponds to a loss of 12.9 per cent of sulphur.

As *boron* compounds are cheap, it was decided to make a few experiments involving the use of this element before proceeding any farther with the rarer materials of the earth's crust. The result of the first set of experiments may be summarized as follows: Boron nitride cannot be produced by heating boron trioxide in a mixture of hydrogen and nitrogen, but if carbon is used as the reducing agent instead of hydrogen, then a certain quantity of nitride is formed. This quantity may be considerably increased if a mixture of carbon and iron, prepared by heating pitch and iron together, was employed instead of the carbon alone. A temperature of about 1,200° C. was used. However, even under the best conditions, only such a small quantity of nitrogen was "fixed" that the method is of no technical importance.

A quantity of boron nitride was prepared by the well-known method of heating a mixture of borax and ammonium chloride. The direct reduction of this nitride was attempted by heating it at various temperatures up to a white heat in a stream of dry hydrogen, but without success. Dry hydrogen sulphide was passed over boron nitride at the highest temperature attainable, using a gas furnace and hard Jena-glass tubing, but they were entirely without action on one another. A still more striking instance of the great stability of boron nitride was shown by passing dry hydrogen chloride over the nitride at a temperature of 1,470° C. The nitride was entirely unaffected by this treatment. From these experiments it is obvious that it is impossible to use boron nitride as a carrier between atmospheric nitrogen and ammonia, as the only reasonable way to obtain ammonia from the nitride is to heat it in a current of steam; but if this is done, it is impossible to re-form the nitride from the trioxide and atmospheric nitrogen, as was demonstrated by the first experiments undertaken with boron.

The next experiments were made with *cerium* nitride, prepared by means of the thermit reaction. The calculated quantity of cerium dioxide was mixed with the equivalent quantity of powdered magnesium and heated in an atmosphere of nitrogen. By this means a mixture consisting principally of cerium nitride and magnesia was obtained. The direct reduction of cerium nitride with hydrogen was tried and it was found that at a dull red heat ammonia was slowly evolved, the cerium combining at the same time with excess of hydrogen forming cerium hydride. Experiments were now performed to find out whether the reverse action could be induced to take place, namely, the conversion of the cerium hydride by means of nitrogen into cerium nitride and ammonia. Cerium hydride was therefore prepared by an exactly analogous method to that used in the preparation of the nitride, namely, by heating a mixture of cerium dioxide and magnesium powder in an atmosphere of hydrogen; this gave a mixture of cerium hydride and magnesia. A rapid current of nitrogen was then passed over the hydride, and the temperature gradually raised to a bright red heat. During the experiment small quantities of ammonia were evolved, while it was subsequently found that the hydride had been converted into nitride. The small yield of ammonia was probably due to the high temperature having decomposed the greater part of it into its elements, for ammonia begins to decompose at 500° C. (Ramsay & Young, Trans. Chem. Soc., 1884.)

On a laboratory scale, and using hydrogen and nitrogen absolutely free from oxygen, carbon monoxide, and water, the oscillation from cerium hydride to cerium nitride and back again can be made to go on indefinitely; during each cycle obtaining hydrogen and nitrogen perfectly free from oxygen

would go far to bar this process from being a commercial success.

Another process of purely theoretical interest could be carried out with vanadium, columbium, or tantalum. It has been shown by von Bolton (*Zeit f. Elektrochemie,* 1905) that the metal is produced if any one of the oxides is heated to a white heat in a vacuum of less than 20 mm. pressure. Nitrogen instantly reacts with the white hot metal giving the nitride (VN). This nitride reacts with steam at 400° C. giving ammonia and the oxide.

Experiments with molybdenum and tungsten were no more successful, as far as working out a "fixing" process was concerned, for although both these elements form nitrides, neither appears capable of combining directly with molecular nitrogen. Working with finely divided tungsten, and at temperatures as high as 1,500° C., no appreciable quantity of nitride was formed.

The elements thus divide themselves naturally into two groups. As an example of the one class may be mentioned the element tungsten, the nitride of which, though directly reducible, cannot be formed directly from its elements; while magnesium, boron, and titanium afford examples of elements which combine directly with nitrogen, but of which nitrides are not reducible directly, so that the only way to obtain ammonia from these nitrides is to act upon them with steam; nevertheless, as these oxides are not reducible, the cycle cannot be completed.

It may be urged at first sight that the experiments with cerium contradict this view; but that is only apparent, for the reduction in this case is probably due to the extraordinary affinity of cerium for hydrogen, which displaces the nitrogen, forming cerium hydride, while the production of ammonia may be looked upon as a secondary reaction in which the displaced and nascent nitrogen combines with the excess of hydrogen present.

Corrosion of Iron.

On page 254 of our July issue we commented on the corrosion of iron as an electrochemical phenomenon, with reference to a paper of Dr. Allerton S. Cushman, before the Society of Testing Materials. This paper has now been published in full as Bulletin No. 30 of the Office of Public Roads of the United States Department of Agriculture. Another paper on the same subject was presented by Dr. William H. Walker, Miss Anna M. Cederholm and Mr. Leavitt N. Bent, in May, before the New York Section of the American Chemical Society, and will be published in full in the *Journal* of the American Chemical Society. We herewith give abstracts of both papers. We also comment on the subject on our editorial pages.

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The paper by Dr. WILLIAM H. WALKER, Miss ANNA M. CEDERHOLM and Mr. LEAVITT N. BENT is an account of an important experimental investigation carried out in the Research Laboratory of Technical Chemistry of the Massachusetts Institute of Technology.

After a review of the carbon-dioxide theory, the electrolytic theory and the hydrogen-peroxide theory of the corrosion of iron, the authors discuss especially the experiments of G. T. Moody, which are believed by this author to prove the correctness of the carbon-dioxide theory. Dr. Walker and his associates have repeated these experiments and confirmed them, but differ strongly from Moody as to the conclusions. Moody's paper was published in the *Journal* Chemical Society (London), 89,720.

The fact that Moody could not detect any rust on iron in pure water without carbon dioxide, is attributed to the fact that Moody's iron had previously been treated by chromic acid,

whereby it had assumed the so-called passive state. Further experiments of Dr. Walker showed conclusively that iron dissolves in pure water free from oxygen and carbon-dioxide. Hence carbon-dioxide is not essential for the corrosion of iron. The experiments on this point are described as follows:

"A round-bottom Jena flask of about 1 liter capacity is inverted on a nozzle supplying live steam for at least 24 hours. This insures the removal of any easily soluble alkalies which would otherwise destroy the neutrality of the liquid. The flask is fitted with a carefully cleaned rubber stopper, through which extends a glass tube drawn down to a moderate sized capillary at its upper end. The flask is three-fourths filled with ordinary distilled water (not conductivity water) which has previously been boiled for several hours in a block-tin heater. The water in the flask is boiled for about 10 minutes, and while steam is still rapidly passing out of the opening the stopper is removed and a piece of bright iron introduced. The stopper is again inserted, the boiling continued for another 10 minutes, and while boiling the capillary is sealed. The flask is allowed to cool after thickly coating the stopper with molten paraffin. If this experiment be carefully performed no action will be observed, the iron remaining bright and the water clear even after standing several days. When the stopper is removed and the water concentrated in a platinum dish, using every precaution to prevent a contamination from dust, a strong test for iron can always be obtained by the use of any of the ordinary reagents.

"Thinking that possibly enough gas had been occluded in the iron to effect the reaction the above experiment was repeated a number of times under conditions which allowed of introducing pieces of iron which had been heated to low redness and cooled in hydrogen. In every case the presence of iron was easily detected when the contents of the flask was evaporated to a few drops.

"This experiment was again repeated with the additional precaution of using water which had been allowed to stand for a number of days over a large quantity of spongy, metallic iron reduced with hydrogen and introduced into the reaction flask by distilling it from the iron in an atmosphere of hydrogen. Notwithstanding all these precautions, a distinct test for iron was obtained after the water had been concentrated.

"We, therefore, support Whitney in his statement that iron will dissolve in water which contains not more than a trace of electrolyte, no oxygen and only that amount of carbon-dioxide which is not retained by strong alkalin hydroxide. In explanation of the failure of the investigators, previously cited, to detect dissolved iron we would state that usually it is not possible to obtain an indication of iron with potassium ferricyanide; for example, in the water as it comes from the flask; concentration generally is necessary."

The authors then describe a direct demonstration of the electrolytic character of the corrosion of iron by means of a special indicator devised by them and Dr. Allerton S. Cushman.

A piece of iron is immersed in ordinary water to which has been added a little phenolphthalein and a trace of potassium ferro-cyanide. Within a very few minutes the iron is seen to divide itself into zones or surfaces which exhibit opposite polarity. Those portions where the iron is anodic become coated with a precipitate of Turnbull's blue, owing to the escape of the iron ions at those points. Those portions on which hydrogen is being liberated, acting as cathodes, become bright red owing to the formation of hydroxyl ions. This action may be more easily studied if this reagent (for which Dr. Cushman has proposed the nome "ferroxyl") be thickened by the addition of natural gelatin or agar-agar. (See below.)

Then follows a particularly interesting part in the paper of Walker and associates, dealing with the function which oxygen plays in the corrosion of iron. Of course, oxygen is necessary for rusting; according to the electrochemical theory the first

action is the passing of iron into the ferrous ionic state, with simultaneous liberation of hydrogen; the ferrous ions are then oxidized to the ferric by oxygen in the atmosphere, with its subsequent precipitation as ferric hydroxide. This is the evident secondary function of oxygen.

But according to Dr. Walker oxygen also has to fulfill a primary function in the corrosion of iron.

The rapidity with which iron will pass into solution in water depends not only upon the electrolytic solution pressure of the iron and hydrogen and the osmotic pressure of the iron ions already in solution, but also upon the "excess voltage" (überspannung) which is required in order that the hydrogen ion which passes from the ionized condition may be set free. In this case there is a counter electromotive force which must be overcome before the hydrogen can be liberated. It is possible, therefore, that the quantity of iron which can dissolve in water is limited to that amount which is equivalent to the hydrogen necessary to polarize that portion of the specimen which acts as the cathode. If this is so, it must be possible to make the solvent action continuous by the addition of any reagent which will dissolve the hydrogen-covered cathode portion.

The matter is made quite clear by the following experimental arrangement of Dr. Walker: Within a jar there are placed two unglazed porcelain cups, acting as porous cups, concentric with each other with the jar. We have, therefore, in the center a cylinder and around it two annular spaces. The three spaces are filled with hundredth-normal KCl, free from oxygen and carbon-dioxide, and the whole is placed upon a hot plate of a temperature to insure continuous boiling. Two pieces of clean, pure iron, joined by an iron wire, are introduced into the central and outside compartments, and the whole while still boiling vigorously is sealed by a metallic cup. Hydrogen is allowed to enter as the jar cools, so as to release and prevent leakage. Such a cell may be maintained for many hours without dissolving enough iron in either compartment to be detected by potassium ferricyanide in its unconcentrated condition. When reduced to a few drops, however, iron may always be shown to be present. Portions of each iron plate may be assumed to be anodic with iron tending to go into the ionized form, and other portions cathodic, being polarized by a film of hydrogen.

If, now, a substance which will dissolve away the hydrogen be added to one compartment, the cathodic portion of the iron contained therein should be depolarized and the action should result in the solution of the anodic portions. Since the two pieces of iron are short-circuited above by a wire and below by the electrolyte, that piece which is continually depolarized would be expected to become the cathode and the other the anode. Hydroxylamine serves as such a depolarizer.

By passing a stream of hydrogen gas through all three cups the boiling and cap may be dispensed with, and iron will not dissolve in 6 hours sufficiently to give directly the ferrocyanide test. If the hydrogen stream in one compartment be replaced by oxygen, iron will immediately begin to dissolve at an appreciable rate in the other compartment, separated though it is by the intermediate compartment through which hydrogen is passing. The dissolved iron in the anode compartment remains in solution as a ferrous salt while the cathode compartment becomes strongly alkaline. If the porous cells be withdrawn the iron at once oxidizes and is precipitated as brown ferric hydroxide.

The primary function of oxygen in the corrosion of iron is, therefore, to depolarize those cathodic portions of the iron upon which hydrogen tends to precipitate.

The influence of the depolarizing action of oxygen may be conveniently studied by using the ferroxyl indicator. For example, in a beaker may be placed a porous earthenware cell and the whole filled with ordinary water containing phenolphthalein and a very little ferricyanide. If a piece of iron be placed within the cell and connected by means of an iron wire

with a piece of platinum in the outside compartment, immediate action takes place, deep red appearing on the platinum and a coating of blue precipitating on the iron. If, however, the platinum be heated in an alkaline pyrogallate solution, washed in boiling distilled water, and while wet used as the cathode in the cell, no action will take place for a number of hours. Only as the platinum takes up oxygen from the atmosphere does the reaction become apparent.

Another conception which differs only in the point of view from the above is to consider the metal which acts as a cathode, for example, the platinum, as an oxygen electrode, and that the current flowing through the circuit (on account of which the iron dissolves) is due to the solution of the oxygen and the formation of hydroxyl ions charging the solution negatively, and thereby requiring a solution of iron at the other electrode to bring about electrostatic equilibrium. When viewed in either of these two lights the action should be proportional to the concentration of oxygen in the solution, and, hence, according to the laws of Henry and Dalton, to the partial pressure of the oxygen in the atmosphere above the solution. This conclusion was indeed experimentally confirmed by Dr. Walker.

The fact that the accelerating action of increased pressure of oxygen may be looked upon as due to an oxygen electrode, has an interesting bearing upon Dunstan's theory of the intermediate formation of hydrogen peroxide. Richarz and Lonnes (Zeit. f. physik. Chemie, 20, 145) decomposed water saturated with air by passing through it, between platinum electrodes, a current of low electrode density. They found that at the cathode the hydrogen was to a large extent not liberated as such but that it combined with the dissolved oxygen to form hydrogen peroxide. These are exactly the conditions which obtain upon the cathodic portions of iron undergoing corrosion, except that there here we have iron instead of platinum. The appearance of hydrogen peroxide is, therefore, to be expected, provided it can exist on an iron surface.

The formation of hydrogen peroxide if it takes place must, therefore, be considered incidental to and not necessary for corrosion. An electric current can pass between bright iron and iron covered with scale only (1) if the concentration of the hydrogen ions be increased by the presence of an acid, or (2) if oxygen or some other depolarizing substance be present.

If a piece of chemically pure iron, free from mechanical strains and without evident crystallization, be immersed in the ferroxyl indicator, the positive and negative zones will be indicated after a few moments. There appears to be an unequal concentration of oxygen or segregation of oxygen upon the surface which cannot be explained by discernible differences in the character of the surface. If the ferroxyl indicator be removed, the surface cleaned by rubbing with a dry towel and the indicator again applied, the same separation into zones is seen, though in an entirely different configuration. The indicator is apparently a very delicate one and susceptible to changes in equilibrium which up to the present have not been detected.

It is significant that from comparative tests made between samples of iron, which had proven in practice as specially resistant to corrosion, and others which had proven as specially susceptible to corrosion, it was found that areas showing marked differences in potential exist in far greater number upon the surface of the piece of iron subject to corrosion than upon iron which is resistent to corrosion.

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Dr. ALLERTON S. CUSHMAN's paper as published in full as a pamphlet of the Department of Agriculture will be found very interesting reading. The photographs which are reproduced in the pamphlet, representing the cathode and anode zones on corroding iron surfaces as indicated by the ferroxyl reagent, are very pretty, but it is to be regretted that they are not reproduced as colored tables.

Dr. Cushman's paper begins with a review of the different theories of the corrosion of iron and criticisms of Moody's experiments. Like Dr. Walker, Dr. Cushman considers that Moody's experiments are not a conclusive proof of the carbonic-acid theory. With respect to the electrolytic theory he points out that since iron has been shown to rust in the presence of pure water and oxygen alone, and since according to the electrolytic theory the corrosion by oxygen is a secondary process, the assumption of electrolytic action as a fundamental cause of the wet oxidation of iron must stand or fall on the determination of one crucial question, namely, whether iron passes into solution even to the slightest extent in pure water. Like Dr. Walker, Dr. Cushman has been able to confirm experimentally Whitney's result that this fundamental question must be answered in the affirmative.

In discussing the stimulating and inhibiting effects of certain substances on the corrosion of iron the rationale of the protective effect of chromic acid and potassium bichromate is discussed at length. If a rod or strip of bright iron or steel is immersed for a few hours in a strong (5 to 10 per cent) solution of potassium bichromate, and is then removed and thoroughly washed, a certain change has been produced on the surface of the metal. The surface may be thoroughly washed and wiped with a clean cloth without disturbing this new surface condition. No visible change has been effected, for the polished surfaces examined under the microscope appear to be untouched. If, however, the polished strips are immersed in water it will be found that rusting is inhibited. An ordinary untreated polished specimen of steel will show rusting in a few minutes when immersed in the ordinary distilled water of the laboratory. Chromated specimens will stand immersion for varying lengths of time before rust appears. In some cases it is a matter of hours, in others of days or even weeks before the inhibiting effect is overcome.

Dr. Cushman shows why the formation of a protective thin film of either oxide or chromate on the surface of the iron is not a satisfactory explanation. On the other hand, it is a fact that if polished iron is allowed to stand for some time in standard tenth-normal potassium bichromate solution, the oxidizing strength of the latter, as measured by its titration value, is slightly reduced without the solution of the iron or the production of any visible effect. Under the same conditions a standard solution of neutral potassium chromate is slightly reduced with the appearance of a small amount of chromic hydroxide. In fact, all the evidence obtainable points to the abstraction by the iron of some of the available oxygen of chromic acid and its salts without the formation or solution of iron oxide films.

Dr. Cushman believes that the passivity of iron is best explained as a "polarization effect produced by the separation and retention of oxygen on the surface of the metal." The iron is brought to the condition of an "oxygen electrode."

The second part of the paper is devoted to the demonstration of electrolytic action in the corrosion of iron by means of the ferroxyl indicator. "Many persons who are interested in the metallurgical problems connected with the iron and steel industry may not be familiar with the modern theory of indicators. and therefore an explanation of the manner in which phenolphthalein shows the presence of hydroxyl ions by the formation of a pink color will not be out of place. Phthalic acid was first prepared by Laurent in 1836 by the oxidation of napthalene, and was first called napthalinic acid. It was afterwards shown that the compound was not directly related to the napthalene structure and Laurent changed the name to phthalic acid, the derivatives of which became known later as phthaleins. Phenolphthalein is a product which is formed by the condensation of two molecules of phenol or carbolic acid with the anhydride of phthalic acid. It is in its nature so weak an acid that it is not dissociated in solution, and as the molecule is colorless, no color is seen when it is added to a perfectly neutral solution. If, however, an alkali is added the corresponding salt of the weak acid is formed, which immediately dissociates with the formation of a colorless metallic cation and the strongly rose-colored organic anion. Thus all hydroxides of basic elements will show the pink color in solution, even when present in only the slightest excess. On this account phenolphthalein is an exceedingly delicate indicator of the presence of hydroxyl ions." Dr. Cushman proposes to call it phenolin.

At a suggestion of Dr. W. H. Walker a trace of potassium ferricyanide is added to the reacting solution, in order to furnish an indicator for the ferrous ions whose appearance mark the positive poles. If iron goes into solution, ferrous ions must appear, which, with ferricyanide, form the well-known Turnbull's blue compound. Going a step further, Walker suggested stiffening the reagent with gelatine and agar-agar, so as to prevent diffusion and preserve the effects produced. This combined reagent is called ferroxyl and prepared and used as follows: "A hot solution of the purest agar-agar or gelatine in distilled water is carefully neutralized with one-hundredth normal potassium hydroxide, using phenolphthalein as the indicator. When exact neutrality has been obtained a few drops of a dilute solution of potassium ferricyanide is added. When a layer of the reagent is poured into a dry Petri dish floating in ice water it should stiffen into a firm jelly in a few minutes. The polished specimens are laid carefully on the jelly and flooded with another layer of the reagent. After the preparation has hardened it should be covered and set away in a cool. dark place. In the course of a few hours the negative and positive zones will begin to develop in red and blue. If the reagent has been properly prepared the color effects are strong and beautiful. In the course of a few days the maximum degree of beauty in the colors is obtained, after which gradual deterioration sets in." The blue areas which appear represent the positive nodes while the pink areas represent the negative nodes, so that these two nodes represent the two electrodes of the short-circuited galvanic cell which causes the solution of the iron with subsequent rust formation.

While some samples of corroding iron show localized electytic action, as indicated by deep pitting, others become covered with a more or less homogeneous coating of hydroxide. which shows little or no tendency to localize in spots or nodes. The underlying reason for this behavior is explained by the use of the ferroxyl indicator. In the first case the positive and the negative poles of the short-circuited couple remain at their place. At the anode iron continually passes into solution, and the surface is pitted, while at the cathode hydrogen is set free. The ferrous ions in solution near the anode are rapidly oxidized to a loose colloidal form of ferric hydroxide. According to whether a negative zone surrounds the positive pole or a positive zone surrounds a negative pole we have to expect the piling up of rust in a crater formation with the metal eaten out at the center or the piling up of rust in a cone at the center with the metal being eaten up around it. That this really takes place is shown by means of micro-photographs.

In the other case in which iron becomes covered all over with a somewhat homogeneous coating of hydroxide, the investigation with the ferroxyl indicator shows that we have to do with an electric system in which the poles change from time to time. What was first anode becomes later cathode and what was before cathode becomes anode.

The best demonstration that the rusting and corrosion of iron and steel in all its forms is essentially an electrolytic phenomenon is afforded by the fact that it has not as yet been possible to find a specimen of such purity that no trace of positive and negative nodes will be formed in the ferroxyl indicator.

There are two possibilities to inhibit rusting. The first is to make the iron so pure and to guard against homogeneity and bad segregation to such an extent that couples are not likely to be formed. The second method is to use the present com-

mercial iron and steel and protect it by a coating such as a dilute solution containing bichromate.

The experiment has been made by Dr. Cushman of keeping iron and steel in dilute boiling solutions of bichromate for protracted periods at the same time that a current of air was bubbling through the boiler, and as long as the strength of the solution was equal to or above one one-hundred and sixtieth normal no rusting has ever taken place. Since this strength is approximately equivalent to 1 pound of the salt in 1,500 gallons of water, there seems to be no reason why potassium bichromate should not come into use as a boiler protective. The application of the various inhibitors in the priming coats of paints and other protective coverings has already been to some extent made use of, and it would appear that slightly soluble chromates should be theoretically the best protectives for the first application to iron and steel surfaces.

"Although it is true that laboratory tests are frequently unsuccessful in imitating the conditions in service, it nevertheless appears that chromic acid and its salts should under certain circumstances come into use to inhibit extremely rapid corrosion by electrolysis."

The Heat Content of Iron.

Dr-Engineer P. Oberhoffer contributes to *Metallurgie* of June 22, July 8 and 22, the full story of his researches on the specific heat of iron. It is a pity that some of Prof. Burgess' pure electrolytic iron was not used; instead, some soft steel from Krupp's was used, containing 0.06 carbon, 0.005 silicon,

ENERGY CONTENT OF IRON.
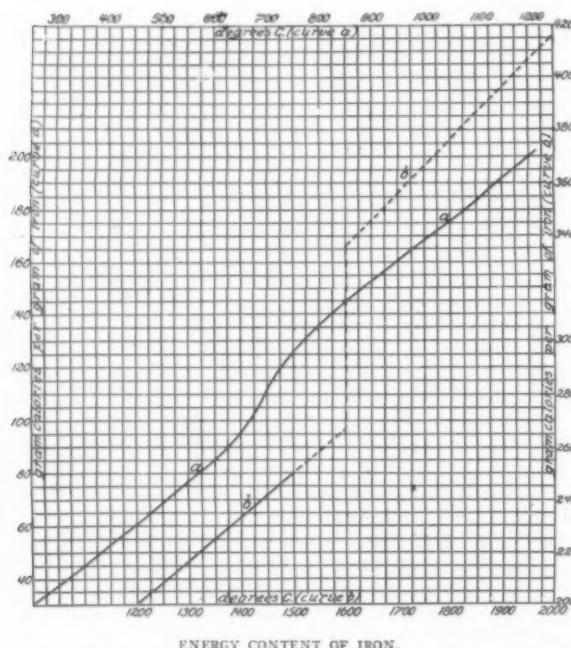
(Curve *b* is the continuation of curve *a*. The scales for curve *a* are at the left and the top; the scales for curve *b* are at the right and the bottom.)

0.005 phosphorus, 0.019 sulphur, and 0.05 per cent manganese. Cooling curves showed arrests in the speed of cooling culminating at 860°, 750° and 680° C.

The specimens were heated in a vacuum, and the heat unit is referred to water at room temperature. The results showed the specific heat of alpha iron to increase regularly, while that of gamma iron is practically constant, thus supporting the earlier determinations of Pionchon.

The actual results obtained by Oberhoffer are given in the

following table, and are plotted in the annexed diagram, showing the gram calories contained per gram of iron:

	Cal.		Cal.
250°	30.5	1200°	200.0
300°	37.7	1250°	208.3
350°	45.0	1300°	261.1
400°	52.2	1350°	224.2
450°	60.3	1400°	233.1
500°	68.3	1450°	241.4
550°	76.7	1500°	250.0
600°	85.0	1550°	258.3
650°	95.1	1600°	266.7
700°	111.8	1600°	336.
750°	125.6	1650°	346.
800°	135.8	1700°	356.
850°	144.4	1750°	366.
900°	152.8	1800°	376.
950°	160.4	1850°	386.
1000°	167.8	1900°	396.
1050°	175.4	1950°	406.
1100°	183.0	2000°	416.
1150°	191.7		

The inferences to be drawn from these figures are interesting and important.

First, we notice that the specific heat of iron rises from about 0.11 at zero to 0.144 at 250°, and to 0.166 at 600°; that between 650 and 700 there is an absorption of latent heat of about 10 Calories; again, about 750°, there is absorption of 7 Calories. About 850° there may be an absorption of 2 Calories, but the observation is somewhat doubtful. Above 900 the specific heat is nearly constant at 0.167. It is a curious fact that from 1.000° up to 1,500° the amount of heat in the iron, reckoned from 0°, is almost exactly 0.167t; i. e., Sm to 0° is 0.167.

The figures above 1,500° (represented in the diagram by a dotted line) are estimated values which we have added to Oberhoffer's observations. Up to 1,600°, the assumed melting point, we have extended the last observation of the last paragraph, making Q = 0.167t. At the melting point we have taken the latent heat of fusion as lying between 69 and 70 Calories. The calculation of this quantity on thermochemical principles is too long to insert here, but may be found fully explained by J. W. Richards in the *Journal* of the Franklin Institute, May, 1897. This makes the heat in just melted iron 336 Calories.

From this temperature on the iron is liquid, and since the solid iron just before melting has a constant specific heat of 0.167, the specific heat of the liquid iron will in all probability (from analogy with other metals) be also constant and probably only slightly higher than in the solid state. We have completed the curve to 2,000°, using a specific heat of 0.20 for the liquid iron.

We think, from a close study of Oberhoffer's work, that he has probably given us the most accurate figures yet obtained for the heat in pure iron, and rounding out his observations by the probable values given and explained; we think these figures altogether are the most accurate which are at present available for use in the metallurgy of iron.　Jos. W. Richards.

Electric Bleaching of Flour in England.—An interesting case with regard to an electric process for bleaching flour was recently decided in the London law courts, as noticed in London *Electrical Engineering*. The Alsop flour-bleaching process consists in passing a current of air through a chamber containing an electric arc, and thence through the flour to be bleached. The British patent covering this process has been revoked. The judge held that the bleaching agent was the oxides of nitrogen generated, and that flour bleaching by means of these gases did not constitute any novelty.

The Electrothermic Reduction of Iron Ores.

By Albert E. Greene and Frank S. MacGregor.

This paper contains the results of an experimental investigation which was carried out by the authors in the electrochemical laboratory of the Massachusetts Institute of Technology on the electrothermic reduction of iron ores containing titanium. To Prof. Goodwin, under whose direction the research was undertaken, we desire to express our warm thanks for the facilities put at our disposal and for the assistance and encouragement which he has given us throughout the progress of our work.

Investigations[1] up to the present time have demonstrated that iron ore can be economically smelted in the electric furnace where power is cheap; they have shown that the electric furnace does not differ essentially from the blast furnace from the metallurgical point of view; and, furthermore, that it has certain advantages in the regulation of temperature and localization of heat, which make it especially applicable for smelting refractory ores and for making special varieties of pig iron.

There are many phases of the problem, however, regarding which data are entirely lacking at the present time, and it was with the hope of making a contribution to certain of these that the following investigation was undertaken. The points to which we particularly directed our attention were:

1. The design and construction of an experimental electric furnace of about 30-kw. capacity.

2. The measurement of the temperature of the molten charge.

3. The factors affecting the temperature and the methods of regulating it.

4. The effect of temperature and of composition of charge on the quality of iron produced.

5. The calculation of the amount of electric energy required per ton of pig iron.

In planning our investigation it was necessary to start out with very little data regarding the best size and shape of the furnace, the character of materials to be used and the details of application of power, etc. The procedure followed was first to build the furnace, making its size and shape conform to the condition of power at our disposal, then to make preliminary runs with one of the Pacific Coast sands, of which a considerable amount was on hand. We thus obtained a working knowledge of the furnace, method of measuring temperature, etc., after which we proceeded to make runs on the regular iron ores, in which (a) the temperature was varied, keeping the charge constant, and (b) the charge itself was varied.

Ores Investigated.

Three samples of ore were obtained with which to carry out the investigation. Two of these were iron sands from the Pacific Coast, and the other was a titanium iron ore from Essex County, N. Y. The sands were used in the first six preliminary runs designed to test the best method of operating this furnace and measuring its temperature. They did not lead to conclusive results concerning their own possible value as a source of iron.

The ore upon which the results of this investigation are based contained practically no sulphur or phosphorus, its analysis being

Fe_2O_3	70.40%
SiO_2	1.99%
TiO_2	26.40%
Al_2O_3	Small
MnO_2	Small
Total iron	52.52%

It was crushed to about ¼ inch in a Blake crusher in

[1] See especially the two reports by Dr. E. Haanel, this journal, vol. III., p. 479, and vol. IV., pp. 124 and 265.

preparation for the furnace. The best grade of Pocahontas coke was used as reducing agent, and the flux was burned lime used in the laboratories of the Institute, and consisted of almost pure CaO. No analysis of either coke or lime was made. These materials were used throughout all the tests.


section EF

section AB section CD

carborundum brick graphite
fire brick carbon
cast iron carbon past

O —— scale —— 1ft.
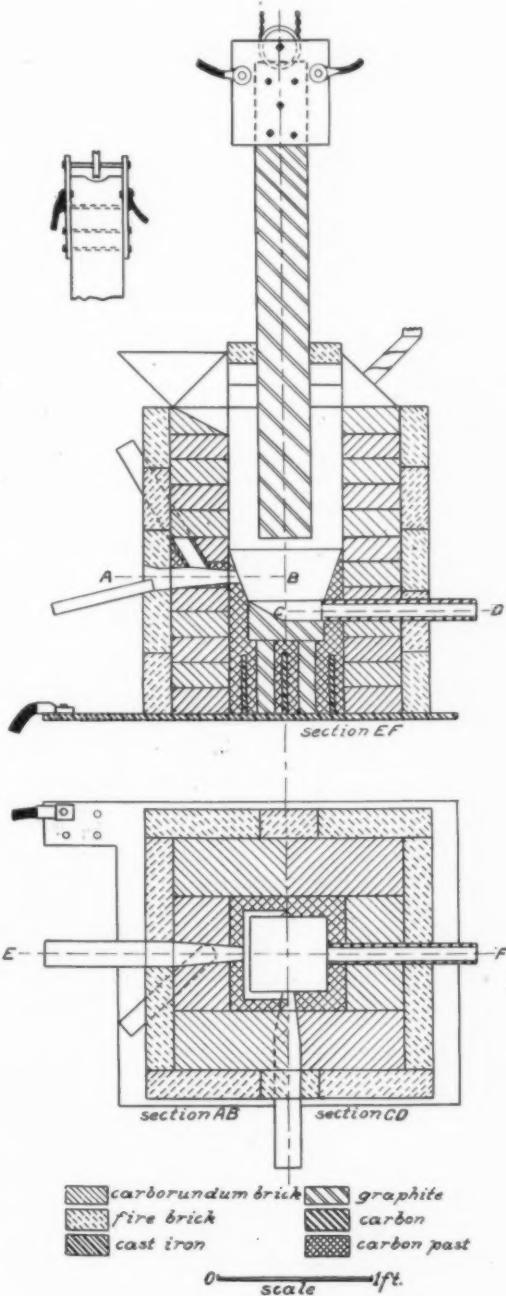
FIG. 1.—EXPERIMENTAL ELECTRIC FURNACE.

Apparatus.

The power used in our experiments was alternating current. It was generated in a special 1,100-volt, 133-cycle, 30-kw. generator, belt driven by a 50 hp. direct-current motor, supplied with power from the power plant of the Institute. The energy was transmitted at 1,100 volts to the transformer in the furnace laboratory, from which it could be taken at voltages varying

from 10 to 160 volts and applied directly to the furnace. [The diagram of connections may be seen in plate.]

The electrical instruments used for measuring current, volts, etc.. were an ammeter, A. C., 5 amps; a voltmeter, A. C., 65 volts; a wattmeter, A. C., 5 amps. and 65 volts; a current transformer; a voltmeter, D. C., 15 volts, and a galvanometer for the thermo-electric pyrometer.

The A. C. instruments were all General Electric instruments. They were not recalibrated, because the precision of the power measurements did not require it.

The temperature of the molten bath was measured by means of a Wanner optical pyrometer reading from 0° to 4,000° C. This instrument was calibrated at the Reichsanstalt, at Charlottenburg, Germany. The standard 6-volt lamp was supplied with current from a storage battery. This voltage was maintained constant by means of a slide-wire resistance in series with the lamp between the mains of the battery, and was read on the 15-volt Weston voltmeter.

A thermoelectric couple was used for getting the temperature of the gases. In stating results all temperatures are given in degrees centigrade and all weights in kilograms.

DESCRIPTION OF FURNACE.

The furnace was first constructed as follows: A plate of iron three-quarters of an inch thick was cast in the form of a rectangle 28 inches x 24 inches. A tongue 4 inches x 6 inches projected at one corner to which cables to the transformer were fastened. In the center portions of the plate five holes, $\frac{3}{8}$ inch in diameter. were bored $2\frac{1}{2}$ inches apart. Into these were firmly driven five iron rods 2 inches long, to aid the conduction of the current from the bed-plate into the crucible. which was to act as one electrode.

Carborundum bricks were laid in this cement around these rods, forming an enclosure 9 inches square and 9 inches deep. This space was filled with a mixture of granular coke and molasses, and the first crucible formed of this mass. Carborundum bricks were used to complete the crucible, around which a layer of fire-bricks was then placed, forming the outside of the furnace. Iron straps and bolts were used to fasten the furnace together.

A tap-hole for metal was placed on one side of the furnace, and on an adjacent side, about 2 inches above the metal hole, was placed a tap-hole for the slag. Conical carbon rods were used to form the tap-holes and also as plugs during the runs.

The other electrode was movable and consisted of a graphite bar 4 inches x 4 inches x 40 inches. The holder consisted of two brass plates, bolted to opposite sides of the electrode by bolts running through the electrode itself. The plates projected above the end of the electrodes so as to support a small grooved pulley. An iron chain fastened to a crane gave an easy adjustment of the electrode, which could either be lowered to the bottom of the crucible or hoisted above the top. Four flexible copper cables were bolted to the supporting plates forming the other electrical connections.

On one side of the top of the furnace was placed a hopper for holding the charge, and the rest of the top was enclosed so as to enable the gases given off through a flue to be collected and analyzed as well as to determine their temperature. The information obtained from the first six runs caused us to introduce various changes in the crucible, and after many ma-

terials were used as a lining, flour carbon and molasses was found to give the most permanent and satisfactory results. Owing to the poor electrical conductivity of the coke paste a graphite block was finally used as crucible base, the block resting directly upon the metal bed-plate. The shape of the crucible was that of a frustum of a pyramid, the sloping walls extending upward about 8 inches, the rest of the wall being the carborundum bricks.

The dimensions of the furnace and crucible as finally used are as follows:

Height of furnace.....................	24 inches.	
Length of side........................	23	"
Depth of crucible....................	8	"
Size of upper portions of crucible,......	9	" square.
Size of base.........................	5	" "
Distance from bottom of crucible to top of furnace....................	15¼	"

MEASUREMENT OF TEMPERATURE.

The development of a suitable method for obtaining the temperature of the molten charges, at the same time keeping the top of the furnace closed, required much experimenting. In the first runs the pyrometer was sighted through a carbon tube 1 inch internal diameter and 12 inches long, which was introduced diagonally through the furnace from the outside, into the molten charge. This was abandoned, as the molten mass solidified in the tube. In run No. 2 a thin carbon plug was put in the lower end of the tube mentioned above, but this did not attain the same temperature as the charge. In run No. 3 a carbon tube, closed at one end, was placed horizontally
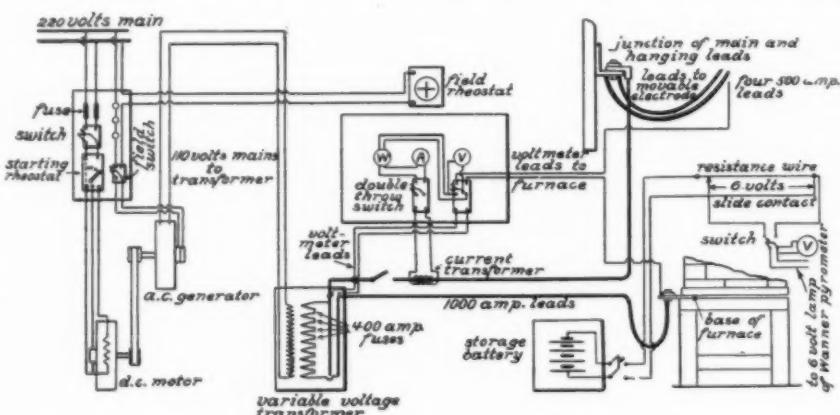

FIG. 2.—DIAGRAM OF CONNECTIONS.

through the furnace walls, so that the end formed a part of the base of the crucible itself.

With this arrangement the molten metal was in direct contact with the surface upon which the pyrometer was focused. As a check on observations made by this method another tube was so arranged with respect to the slag hole that when the plug was removed it would give a view of the outflowing slag just as it left the interior and before it reached the open air.

Readings by these methods checked well, but at times the plug became covered on the inside with a solid film, which had to be removed by poking. Later, owing to lack of time, when it became necessary to abandon the work on the gases the method of measuring the temperature was much simplified. With the furnace top partially open it was only necessary to sight the pyrometer upon a clear area made in the surface of the molten charge.

The five methods which we tried of determining the temperature of the molten zone were, therefore (1), open tube entering top of molten slag; (2) plugged tube entering top of molten slag; (3) horizontal plugged tube entering near base

of crucible; (4) open tube giving a view of outflowing slag just leaving interior; (5) using surface of charge as seen from the top of the furnace.

Of these the third seems the most satisfactory for a closed-top furnace; for an open-top experimental furnace no larger than that which we used the fifth method may also be used.

The primary factor in the temperature regulation is the amount of electrical energy put in. This is dependent on three things: the voltage, the current and the height of the electrode. In the first six runs the relation between temperature and these factors, taken separately, was more easily observed than in later runs, because of the large amount of slag present
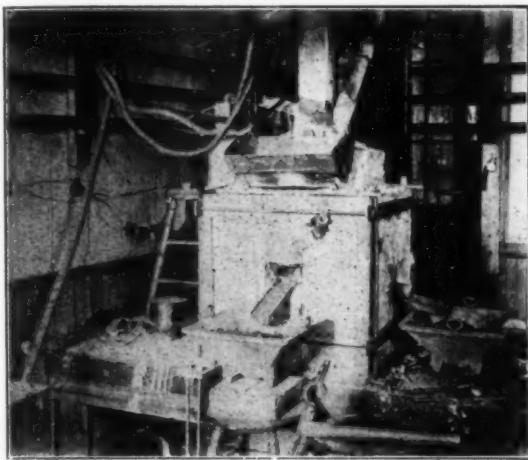
FIG. 3.—VIEW OF ELECTRIC FURNACE.

and the greater length of run, but these first runs did not give good working results and served mostly to show the mechanical action of the furnace and the above points. A wattmeter was used after run No. 5, showing the relation of power input and power factor.

The following points may be noted: The current tends to increase when no addition of charge or other change in conditions is made. This was most clearly shown in one of the runs where, to begin with, the current at 4.30 P. M. was 660 amps., and it increased to 810 amps in 12 minutes at 4.43 P. M. without any external change in height of electrode. This is probably explained by the fact that the charge became entirely molten and the electrical energy used in melting it served next to raise its temperature and therefore its conductivity.

The result of change of electrical input was most easily observed in run No. 6. At 3.15 P. M. the power input was increased from 16.5 kw. to 19.2 kw.; the temperature before the change was 1,204° C., at 1 minute after 1,222° C., 2 minutes after it became practically constant at 1,234° C. These facts show the readiness and ease with which the temperature may be regulated.

The power factor in our apparatus was approximately constant at 92 per cent. The best regulation for constant temperature was obtained in runs No. 13 and No. 14 by maintaining the input constant. Our experience shows that the temperature may be regulated by the energy input, by the current or voltage, and to a certain extent by the height of electrode, and that the temperature responds very quickly to these changes.

To maintain constant temperature with a constant rate of input of charge, the energy input must also be constant.

DESCRIPTION OF TESTS AND RESULTS.

First. A series of six runs were made on one of the iron sands from the Pacific Coast. They did not furnish any definite information except as to means of measuring and

regulating the temperature, and the details of these runs will therefore be omitted.

In runs from No. 7 to No. 14 the titanium-iron was made the basis of tests and a summary of the results of these runs is given below:

Run No. 7.   Ore Treated—Titanium-Iron Ore.

The composition of the charge for this run was:

Ore	10 kgs.
Lime	2.28 "
Carbon	2.25 "
Length of run	55.0 minutes.
Mean volts on furnace	23.7
Mean amperes	736
Mean kilowatts	16.0
Power factor	941
Working temperature	1,393°
Weight of metal in kgs.	1.32
Weight of slag in kgs.	4.03
Horsepower-years required per ton of pig	1.14

This run was made with a very basic slag at a comparatively low temperature, 1,393°, and the metal produced was analyzed for Si and Ti, while the slag was analyzed for iron.

The furnace was heated for about an hour before charging. The size of the reducing agent was increased from what it had been in previous runs to about ¼ inch, owing to the large loss of fine powder by burning in the upper part of the furnace.

The measurements of temperature in the furnace and of the
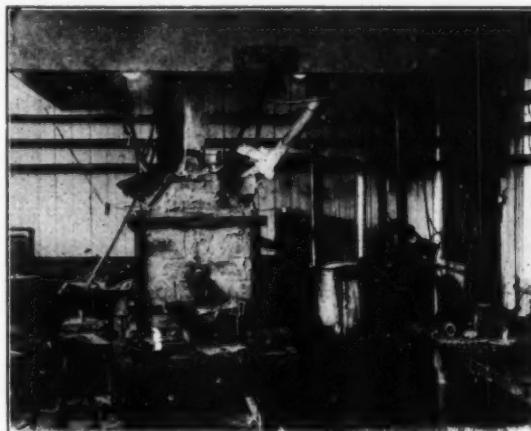
FIG. 4.—VIEW OF ELECTRIC FURNACE.

outflowing slag checked fairly well. The slag was quite fluid and the furnace emptied easily.

Run No. 10.

Composition of charge same as in run No. 7.

Length of run	53 minutes.
Mean volts on furnace	28.4
Mean amperes	763
Mean kilowatts	20.8
Power factor	.928
Maximum temperature	1,593
Weight of metal produced in kgs.	1.13
Weight of slag produced in kgs.	1.60
Horsepower-years per ton of pig	2.25

In runs 8 and 9 the temperature readings were unsatisfactory. In run 10, as was intended, the same charge as used in run No. 7 was smelted at a higher temperature, and as before analyses of the products were made for Si and Ti in the metal and Fe in the slag.

It was decided next to change the composition of the charge, making it more basic. This was done in run No. 11.

Run No. 11.

Composition of charge:

Ore	10 kgs.
Lime	3.5 "
Coke	2.25
Length of run	31 minutes.
Mean volts on furnace	24
Mean amperes	1,038
Mean kilowatts	22.71
Power factor	.910
Maximum temperature	1,549
Weight of metal kgs	1.60
Weight of slag	.90
Horsepower-years per ton of pig	.97

The slag obtained in this run was quite infusible and would not run. This is probably due to the high lime content of the charge. The samples of metal obtained in runs No. 7 and No. 10, as well as in this run, were very hard and somewhat brittle. They did not have any blow-holes but contained graphite. No analyses for carbon were made, and it was impossible to investigate the effect of temperature on the carbon content because of lack of time. The metal and slag were analyzed as before.

Run No. 12.

Composition of charge same as in run No. 11.

Length of run	29 minutes.
Mean volts on furnace	31.1
Mean amperes on furnace	822
Mean kilowatts	23.8
Power factor	.928
Maximum temperature	1,655°
Weight of metal kgs	1.77
Weight of slag	2.27
Horsepower-years per ton of pig	.93
Total carbon in metal	3.40%

The carbon content of the metal in this run was determined and found to be 3.40 per cent. In this and previous runs the furnace top had been closed in order to collect samples of the gas and measure its temperature. This scheme was abandoned in further runs. It was next planned to smelt a charge very low in lime at the highest temperature obtainable with the power at disposal.

The metal obtained was finer grained than before and more malleable. The slag was more fluid than in run No. 11.

Run No. 13.

Composition of charge:

Ore	4 kgs.
Lime	0.3
Coke	.94
Length of run	24 minutes.
Mean volts on furnace	24.0
Mean amperes	1,005
Mean kilowatts	23.2
Power factor	.964
Maximum temperature	1,922°
Weight of metal in kgs	1.09
Weight of slag in kgs	1.71
Horsepower-years per ton of pig	1.22

Run No. 14.

Composition of charge same as in No. 13.

Length of run	12 minutes.
Mean volts on furnace	21.5
Mean amperes	811
Mean kilowatts	16.15
Power factor	.922
Maximum temperature	1,469
Weight of metal kgs	.605
Weight of slag kgs	1,365
Horsepower-years per ton of pig	.745

In the last two runs the best regulation of temperature was obtained. This was partly due to the good shape and the character of the crucible. The highest temperature obtained throughout the tests was in run No. 13, where the regulation of the temperature was very satisfactorily accomplished by decreasing the voltage and therefore the power.

The slags in these two runs were both very fluid, and the charge at the lower temperature did not seem to be more difficult to fuse or less fluid than the same charge at the higher temperature. There was a difference in the appearance of the metal reduced at the two temperatures, that at the higher having a fine fracture with blow-holes, while that at the lower temperature crystallized and contained a good deal of graphite.

The results of the analyses of the products of the last six runs, the composition of the charge, the quality of slag, temperature and electrical input are tabulated as follows:

Run No.	Ratio $\dfrac{CaO}{Al_2O_3 + SiO_2 + TiO_2}$	Per Cent. SiO$_2$ in Metal.	Per Cent. Ti. in Metal.	Per Cent. Fe. in Slag.	Temperature of Molten Charge Degrees C.	Quality of Slag	Electric H.P. Years per Ton of Pig.
7	$\dfrac{2.25}{2.90}$	0.10	0.00	2.95	1375	Medium fluid	1.14
10	"	0.11	0.00	7.10	1593	Fluid	2.25
11	$\dfrac{3.50}{2.90}$	0.13	0.00	6.37	1549	Infusible and viscous	0.97
12	"	0.23	0.00	7.56	1675	Infusible and viscous	0.93
13	$\dfrac{.75}{2.90}$	0.30	0.20	...	1922	Very fluid	1.22
14	"	0.44	0.04	....	1469	Very fluid	.79

The results of the tests on the reduction of SiO$_2$ show, as would be expected, that the reduction increases with the temperature, but general conclusions as to the amount of SiO$_2$ that would be reduced at other temperatures cannot be drawn from these tests owing to the lack of sufficient data.

The analyses show that for a given charge the amount of iron slagged off increases with the temperature; increasing the temperature therefore tends to have the opposite effect to increasing the basicity of the charge.

The conditions under which the reduction of titanium ore to the metal begins are very important for the smelting of such ores. It was with the intention of determining these conditions that the great variation in lime content of the charge was made and the results were successful. The analyses of the reduced metal show that no titanium was reduced until the lime content of the slag was made small. In run No. 13 the ratio of the weight of CaO in the charge to the Al$_2$O$_3$ +

SiO$_2$ + TiO$_2$ was $\dfrac{.75}{2.90}$, and at the temperature 1,922° of this run the amount of titanium in the metal was 0.22 per cent. At the lower temperature 1,469° of run 14, but using the same charge, only 0.04 per cent was found in the metal.

In none of the previous runs in which a higher per cent of lime was used in the charge was titanium reduced at all. The tests indicate, therefore, the character of the charge and the temperature limits for which no reduction of titanium takes place.

The observations on electrical input were not primarily taken with the idea of obtaining data on the efficiency of the electric furnace, but rather to show the relations between power input and the resulting temperature; nevertheless, the results are very good when the small size and relatively large radiating

surface of the furnace are considered. The lowest amount of energy required in any run per ton of metal reduced was found to be 0.75 electric horsepower-years.

The results of run No. 13 show that in order to smelt a charge at 1,922° C., the amount of electrical energy required in excess of that needed to smelt the same charge at a temperature 453° C. lower was 0.475 electric horsepower-years. It is probably quite accurate, because the run at the lower temperature was made immediately after that at the higher temperature, so that the reduction should be approximately constant. These facts should hold then for the same charge in a larger furnace.

Owing to lack of time further data, making possible the calculations of the amounts of heat required at the two temperatures were not obtained. The field for experimental work along the line followed in the tests is very broad, and it is to be hoped that the work may be extended in the near future.

Massachusetts Institute of Technology. Boston, Mass.

Transmutation of Elements.

So many remarkable statements have been recently published in the daily papers on the alleged experimental transmutation of copper into lithium by Sir William Ramsay that it is interesting to give herewith an abstract of his paper read on Aug. 2 before the British Association for the Advancement of Science. The paper was entitled "On the Variability in the Products Resulting from Changes in Radium Emanation." The following abstract is taken from the London *Electrician*, Aug. 9:

The author commenced by reminding his audience that radium, actinium and thorium all yield helium, and then proceeded to describe the results of experiments which are nothing short of remarkable. It is known that the emanation decomposes water with the liberation of excess of hydrogen, but where this excess of hydrogen comes from nobody knows. Sir William Ramsay exposed a solution of copper sulphate to the emanation for about a month, and at the end of that time the residue obtained gave the spectra of both sodium and lithium. The experiments were repeated three times, and the results were perfectly consistent in each case. The presence of sodium was not, of course, surprising, as the containing vessels used were composed of glass, but all the materials were tested for lithium, and there was not a trace before the experiments were commenced. Nevertheless, Sir William Ramsay expressed a doubt as to whether the quantity of sodium found could have all come from the glass, and he is going to undertake further investigations in this direction.

His next experiment was with copper nitrate, when lithium was again detected after a solution had been exposed to the emanation. Fresh copper nitrate not so treated with the emanation showed no sign of the presence of lithium. In both cases, however, sodium sulphate was detected, but the treated substance showed just twice as much (1.6 milligrammes) as the untreated substance. On evaporating water treated with the emanation, 0.3 milligramme of solid was obtained, while the inactive gas produced was neon with a trace of helium. Gases from the treated copper nitrate solution contained argon, with possibly a trace of neon. He remarked that 1 cubic cm. of emanation gives off 3½ million times as much energy as 1 cubic cm. of a mixture of hydrogen and oxygen when exploded, and suggested that some of this vast amount of energy might account for the presence of the elements which he has found.

In the discussion which followed, the Hon. R. J. Strutt confessed that he could not find any source of error in Sir William Ramsay's experiments to account for the presence of neon in the case of water and emanation. He made a rough calculation in order to determine how much air would be required to provide the amount of neon (0.5 cu. mm.) obtained by Sir William, and found that it was about 100 cubic mm. In these circumstances he was sure that there could not have been such a large leakage of air to the apparatus as would account for this quantity. He further mentioned that there was quite sufficient lithium in quartz vessels to give a very distinct spectrum.

Prof. Rutherford complained that the amount of radium in the possession of experimenters was deplorably small. There were only about two laboratories in the world that were in a position to repeat Ramsay's experiments, and if only an experimenter could have a gramme instead of 100 milligrammes at his disposal there would be a very great deal more work done.

Prof. H. E. Armstrong, F. R. S., put forward the suggestion that the so-called inert gases are in reality very active, and that they are not monatomic at all.

In reply, Sir William Ramsay said that helium, when passed through a bath of liquid hydrogen, gave up a considerable amount of krypton.

Notes on Electrochemistry and Metallurgy in Great Britain.

(*From Our Special Correspondent.*)

THE ENGINEERING CONFERENCE OF THE INSTITUTION OF CIVIL ENGINEERS.

MINING AND METALLURGICAL SECTION.

The papers presented solely to this section were mostly concerned with mining matters. The first paper, by Mr. G. A. Denny, dealt with "Problems of the Witwatersrand Goldfields." For deep winding the author inclined to the electrical double-stage system; and he considered that the existing system of stamp mills, with cumbersome tailing and slime treatment plants, was economically and scientifically wrong; and that the future would witness a resort to simple methods of stage crushing, stage grinding, circulation of cyanide solution and final filter pressing. For underground mining he favored the utilization of traveling conveyor belts. Owing to excessive capital costs for shafts—£40 to £50 per foot equipped—each one should command a large mining area. The distances between shafts would in future probably be at least 1 mile. To connect them underground will occupy four years. The problem will be to ventilate the mines during the four years prior to connection. The cross-sectional area of the shafts may be taken as 200 square feet, the average barometer 24½ inches, and mean temperature 61° F. The rock temperature at 4,000 feet on the Rand is estimated at 85° F., a figure much below that of other fields. Mechanical ventilation, at present practically unknown on the fields, must be practiced in future. For power transmission electricity and compressed air are used. The average efficiency secured from the former does not exceed 50 per cent, that of the latter does not exceed 6 per cent. The problem is to raise these efficiencies. For pumping the author inclines to the hydraulic pumping system, though the great advantages to the baler, when small quantities only are to be dealt with, probably render it superior to any system of pumping.

Next came papers by Prof. Henry Louis and Mr. C. E. Rhodes upon the subject of mine shafts. Prof. Louis' paper on "Special Methods of Shaft Sinking" appealed chiefly to coal miners, as it was confined to the means which have to be resorted to when ordinary methods cannot be applied economically on account of excessive influx of water. The largest amount of water successfully sunk through appears to have been at Horden Colliery, where 9,250 gallons of water per minute at a depth of 540 feet were dealt with. When the water-bearing strata are firm ground the Kind-Chaudrom method of boring shafts is mostly used. Since its introduction in 1854 about eighty shafts have been sunk by it, of which five

have been in Great Britain, at the Cannock and Huntington Colliery, at the Whitburn Colliery and at Dover. When the water-bearing ground is running three groups of methods are resorted to, namely, (1) Driving down annular sheet piling; (2) forcing down continuous cylinders of brickwork or iron, and (3) the Poetsch freezing process. The first method is not often seen now, but a good modern example is afforded by the recent sinking at Bowburn Colliery. Ferro-concrete sheet piling, which has never been tried might probably be used. Of the second method there have been several good examples in Scotland, but the principle has reached its greatest development in Germany. The freezing process, which was devised in 1883, has been used repeatedly with success in France and Germany. In Great Britain it has recently been applied in the Durham coal fields at Washington, at Eastington, at Dawdon, and is now in progress at the famous Wearmouth collieries. Finally, reference was made to a method that has been tried in France, the forcing of cement slurry through bore-holes into soft, fissured strata, in order to form a wall of concrete within which sinking can be performed.

Mr. C. E. Rhodes' paper on "The Design and Equipment of Shafts for Deep Winding" was interesting chiefly on the mechanical side.

Mr. E. H. Mann's paper on "Arrangement and Design of Colliery Surface Works" need only be mentioned, because of its account of the use of coke ovens with the employment of gas for driving gas engines coupled to electric generators.

A paper by Mr. J. E. Stead on "Segregation in Steel," both in its contents and in the speakers who discussed the paper, suggested a meeting of the Iron and Steel Institute. Mr. Stead commenced with the following universally accepted views:

"1. That the purer crystallites fall out of solution in advance, leaving a less pure metal liquid, and that at one stage of the gradual solidification the metal is a pasty mass consisting of the purer solid part and an impure liquid portion.

"2. That from some cause or causes some of the more impure liquid is rejected from the surface of the freezing walls in ingots. This ascends and finally lodges under the solid upper crust of the ingots, where it eventually freezes.

"3. That steel which is wild after pouring into the mould is usually badly segregated.

"4. That steel cast at abnormally high temperatures, or what is equivalent, very slowly cooled, favors axial segregation of the impurities. •

"5. That the addition of a small quantity of aluminium to liquid steel, which is practiced by steel makers for the purpose of producing quietness in the mould and soundness in the steel, also reduces axial segregation, a fact admirably demonstrated by Mr. Benjamin Talbot.

"6. That not only does aluminium effect the reduction of axial segregation, but, as is proved by the microstructures of the specimens exhibited, it also almost completely removes the minor or dark spot segregations.

"7. That sulphur segregates the most, whilst phosphorus is intermediate between sulphur and carbon in this respect."

Upon these facts the following hypothetical conclusions were presented:

"1. That as the segregate rejected from the freezing steel is specifically lighter than the liquid steel it will, on that account, float upwards along the freezing walls of the ingot.

"2. That the gases driven off from the freezing walls must accelerate the ascent of the segregate, and therefore anything which will reduce or prevent the elimination of gas must tend to check the rate at which the more impure liquid ascends.

"3. That gas blow-holes, which can only form in the plastic mixture of solid pure crystallites and impure liquid, must exert considerable pressure on the pasty metal, and it seems almost certain that some of the impure liquid will be squeezed out, escape into, and join the liquid adjoining the freezing walls,

and, therefore, under certain conditions, the formation of blow-holes must increase axial segregation.

"4. That because the segregate rises to the top of the still fluid column, there must be a central descending slow current. This current in passing over the very slowly freezing lower part of the ingot, deposits the purer crystallites. The impurer liquid then flows horizontally to the vertical walls and ascends, but as the walls develop and grow out of the liquid facing them, solid layers must be formed richer in impurities than the average steel. In this way I explain the annular rings, or fringes, and the purer metal in the lower central axes.

"5. The rings of independent dark spots are accounted for by the assumption that some of the gas in the blow-holes, after exerting its pressure, escapes, and that a portion of the impure liquid enters and more or less completely fills them. That some of the holes have been found lined with impurer metal is a fact.

"6. The irregularly distributed dark spots may be due to the same cause as is suggested in the last paragraph, and also to the land-locking of the segregate between the branches of the large primary crystals."

In conclusion, Mr. Stead pointed out the difficulty of diagnosing cases of segregation. Very frequently rail failures attributed to sulphur, phosphorus or manganese were due solely to bad laying.

A large number of speakers took part in the discussion, which was opened by Mr. George Ritchie, who agreed with the author in thinking that the segregation was less in sound ingots than in honeycombed ones. The difficulty of securing sound ingots increased with the size of the ingot, and in illustration of his remarks he showed a photograph of a longitudinal section through the center of a huge 20.15-ton fluid compressor ingot made at Beardmore's Parkhead Forge. Mr. Archbutt referred to the effect of segregation in causing discrepancies in analysis. He cited the case of a piece of a rail drilled in twelve places, different analytical results being obtained in each case. Mr. F. W. Harbord disagreed with the author in some of his views. Provided that the temperature of casting is kept under control, segregation was not a serious matter in the case of the highest qualities of steel. Mr. C. P. Sandberg, Jr., considered that, for rails, porosity was a greater danger than segregation. For a complete study of segregation it was necessary to deal with the question from a chemical and physical point of view.

Mr. Stead replied briefly, confessing that the statement that aluminium removes the dark spot segregations, whilst regarded as an acknowledged fact by himself, was not so regarded by everybody. He felt that there was still much ignorance with regard to segregation, and that further research was necessary, which might advantageously be conducted on the lines indicated by Sir Thomas Wrightson.

A joint meeting of the "Mining and Metallurgical Section" and Section VII., "Applications of Electricity," was next held, to listen to Mr. Bertram Blount, *Optimist*, upon "Electro-metallurgy." Mr. Blount's optimism was simply superlative. Not content with describing what had been done in regard to copper refining, he forecasted an electric furnace capable of smelting copper ores. Improvements in the manufacture of aluminium would probably lower the cost and permit its use as freely as zinc. "The largest of all electro-metallurgical industries will be the manufacture of steel. Already steels of high grade can be successfully prepared in electric furnaces of various types—the Héroult and the Kjellin representing two of the most distinctive and promising. Probably, in the first instance, the electrical method will have its greatest measure of success in preparing steels of such high grade that any extra cost will be quite outweighed by the certainty that the metal will absorb no impurity in the course of manufacture. But as methods are cheapened it may well be that every grade of steel now prepared in open-hearth furnaces will be prepared in corresponding furnaces electrically heated. The power

necessary should be obtainable from blast furnace gases, for, after a liberal allowance for heating the blast and for the blowing engines, hoists and subsidiary gear, there is certainly an ample surplus, provided modern power plant is installed. Zinc is a metal not at present smelted electrically, but which for chemical and physical reasons is excellently fitted for production in that manner. There is much the same reason to replace the present furnaces with their numberless small and costly retorts by a furnace internally heated by current, as there is to supersede the older mode of making phosphorus and carbon bisulphide by the electrical methods now in operation.

Of contributions to the discussion only a few need be noted. Mr. McLaren pointed out the important difference which exists between iron and steel smelting to copper smelting; the valuable product in the former case is large, while in the latter it is small. He also called attention to the fact that copper at high temperatures is subject to a certain loss in value.

Prof. Harbord said that the electric furnace was not a competitor of the blast furnace as regards cost. The electric furnace was not a cheap melter but a cheap refiner. He advocated starting with the blast furnace and refining with the electric furnace. He was of opinion that blast furnace gases were of little value for power purposes. In his opinion the value of water power was very much exaggerated; as a rule water power was too intermittent to be of much commercial value. There were, of course, a few exceptional cases. such as Niagara.

Mr. A. A. Campbell Swinton said the subject should be of interest to all electrical engineers wishing to improve their load factors. He mentioned that the Carville power station at Newcastle-on-Tyne was already supplying a considerable load to a neighboring aluminium company, and that the British Aluminium Co. was about to take power from the same station. It would, he thought, pay to supply current at a very low price, as it would have a great effect on the standing charges. An electric furnace was understood to mean heat produced by an electric arc, but Sir William Crookes had shown that the bombardment of cathode rays within a vacuum tube generated intense heat. In a lecture which he, Mr. Swinton, had delivered before a kindred institution, he had shown that this could be employed on a large scale, and he was pleased to hear that Messrs. Siemens Bros. were using the device in connection with the manufacture of electric lamp filaments.

Dr. F. M. Perkin said that the paper did not cover the whole of the electro-metallurgical industries; graphite, calcium carbide and carborundum had, for instance, been omitted. He was aware, however, that its limited length would not allow of everything being dealt with. One reason why so much of the electro-metallurgy work had gone abroad was that engineers and chemists in this country had not worked together. He was interested in the cathode rays system mentioned by Mr. Swinton. He could believe that the system would be successful on a small scale for dealing with tantalum, but the difficulty in adopting the system on a large scale appeared to lie in maintaining a good vacuum.

A paper upon "The Education of Engineering Students, Particularly with Regard to Mining and Metallurgy," by Mr. Walter Rowley, concluded the work of this section.

Shipbuilding.

The dependence of the shipbuilder upon the metallurgist and the value of steel of high tensile strength, formed the subject matter of three papers presented jointly to the Shipbuilding Section and to the Mining and Metallurgical Section.

Mr. A. E. Seaton presented a paper entitled "The Use of High Tensile Steel in Compound Structures, Such as Ships, Bridges, Etc." In 1872, Whitworth offered steel plates of 40 tons per square inch tensile strength and 30 per cent elongation. In 1874-5 Siemens offered 40-ton plates to the Admiralty, which were tough and good. In 1878 merchant ships were being classed which were built of iron whose utmost strength

was 22 tons per square inch and elongation seldom more than 3 per cent, and warships built of iron of 23 tons strength with 5 per cent elongation. Steelmakers then offered a material 20 per cent stronger, with an elongation of 20 per cent, and to bend double when cold instead of snapping after a few degrees, as the iron did. The first bridge to benefit by steel was built by Eads at St. Louis in 1874; the first wholly of steel was the Glasgow Bridge over the Missouri River in 1879.

Since 1896 high-tensile steel has been successfully employed in the construction of destroyers and similar craft. In the Forth Bridge it was used only in compression; to-day there need be no hesitation to put it into tension, and overcome thereby many difficulties. Recently the huge Cunard ships, with their heavy machinery, have been constructed to withstand the stresses of service conditions by freely using the high-tensile steel of Spencer and Colville.

The author was firmly of opinion that high-tensile steel could be used with advantage in spite of its higher price and allegations as to extra cost of working. Upon the latter subject Mr. Seaton declared that this should be little or nothing, for even if it were necessary to drill and plane, instead of punch and shear. with modern tools and special steel it could be done as cheaply. Then this steel could be handled hot or cold just as the mildest steel. The angle-bars of keelsons, stringers and other longitudinals might be of it, as also the angle-bars of deep frames and other analogous stiffeners. The rivets should be of it, or of a steel whose resistance to shear is more than 20 tons, if the utmost advantage is required. Tough high tensile strength steel might be used in place of steel casting.

Mr. A. F. Yarrow contributed the second paper, dealing with "High-Tensile Steel for Torpedoboat Construction." This described the experiences his firm had had in constructing the destroyer "Sokol," in 1894, for the Russian government. The metal used in the hull had a tensile strength of 37 tons to 44 tons per square inch, and an extension of not less than 15 per cent in 8 inches for plates of 3/16 inch thick and over. "I take it," said the author, "our aim should be that all parts of the same structure should offer the maximum resistance simultaneously, and by so doing secure collectively a greater resistance to distortion than if the giving way were at varying periods. I think also the frames should be of high tensile steel, because they would be stiffer to resist distortion. With regard to the riveting of the high-tensile steel plates, in the "Sokol" we increased the rivet area from what we adopted previously to the extent of about 50 per cent. This was arrived at by careful experiment; it was found that the high-tensile steel plates would shear the rivets if there were not a very large margin beyond the usual practice in rivet area—that is, assuming mild steel rivets were used in combination with high-tensile steel plates. The advantage gained by using this class of steel was considerable."

The third paper, by Mr. E. W. de Rissett, upon "The Use of High-Tensile Steel in the Construction of the 'Mauretania.'" stated that at a very early stage, when the stresses and structural strength of this vast and heavily-powered vessel were being considered, it became evident that steel of superior strength, in conjunction with hydraulic riveting, would have to be employed at certain parts to produce a structure which would combine the maximum of strength with the minimum of weight. It was then determined by the builders of the "Mauretania" and sister vessel "Lusitania," in conjunction with the Cunard Co. and the officials at the Admiralty and Lloyds, that high-tensile steel should be employed where the greatest stresses would be encountered, and also in other parts of the structure where steel of this character could be profitably employed to save weight, such steel to have the following qualifications under normal conditions: (1) An ultimate tensile strength of 34 to 38 tons per square inch; (2) an elastic limit of not less than 20 tons per square inch; (3) elongation not less than 20 per cent in 8 inches. In addition it should satisfactorily stand certain physical tests. For plates

¾ inch thick and less it was found that high-carbon steel fulfilled these conditions, but for greater thicknesses silicon steel, supplied by Messrs. J. Spencer & Sons, Newburn, was preferred, as the high-carbon steel of 34 to 38 tons tensile strength proved slightly defective in the elastic limit. During mechanical tests made by Lloyds of the pieces of high-carbon steel in which a single rivet hole had been made, it was observed that to punch the hole ⅛ inch small and rimer it out to full size reduced the strength of the sample less than if the hole had been drilled the full size. At all events they consider they were quite warranted in the face of such evidence in punching the high-tensile steel plates up to ½ inch in thickness with holes ⅛ inch less in diameter, then rimering them out to the full diameter required by the rivet. By punching the holes small and rimering them as described, the saving in labor was about 10s. per plate, or about 30 per cent less than electric drilling. All the holes in high-tensile steel above ½ inch in thickness were drilled, and the rag of the hole was removed by a special tool, which at the same time removed the sharp edge of the hole and produced the requisite taper for the neck of the rivet. High-carbon steel was adopted in all the main transverse and longitudinal bulkheads extending to the upper deck. The lower portions of these are 10/20 inch thick, thence 9/20 inch to lower deck, 7/20 inch to main deck, and above this they are 6/20 inch. The stiffening bars are of ordinary mild steel of channel or angle sections. Silicon steel was used for parts of the top sides and doublings, also for the stringers, decks and doublings on the shelter deck for the full width between the ship's side and casings, and stringer and adjoining strake on upper deck for a width of 8 feet 6 inches, and for a length of about 500 feet amidships on the shelter deck, and about 480 feet on the upper deck, tapering off at the ends. The remainder of the plating to the sides of the casings on the upper deck is of high-tensile carbon steel extending for 400 feet in length. By the employment of high-tensile steel a reduction of 10 per cent on the basis of scantlings of mild steel was allowed, and a corresponding reduction in the thickness of the bulkheads were made of this material. The result had been a saving in weight of about 200 tons with an appreciable increase of strength in the top structure. The silicon and high-carbon steel were not annealed. The edges of seams and butts were planed. The author also pointed out how, in his opinion, a reduction of a further 10 per cent—making 20 per cent in all—might have been made in these vessels. The authorities at Lloyds Registry, from their experience up to date, strongly recommended that the rivets used for the whole structure, including the silicon and high-carbon steel, should be made of mild ingot steel, consequently this material was adopted, special provision being made to minimize the shearing effect on them by rounding the edges of the drilled holes by a special tool, which was also coned to suit the taper neck of the rivet.

THE FARADAY SOCIETY.

The June meeting of this Society, with its four papers and general discussion on "Hydrates in Solution," was only mentioned in my last letter. The papers were as follows:

(1) By Mr. W. R. Bousfield and Dr. T. M. Lowry on "Thermochemistry of Electrolytes"; (2) by Dr. J. C. Philip, on "Hydrates in Solution"; (3) by Dr. G. Senter, on "Methods for Determining the Degree of Hydration"; and (4) by Dr. A. Findlay, on "The Stability of Hydrates."

The discussion was relatively brief. Prof. W. A. Tilden, F. R. S., referred to the fact that in crystals it appeared to be the metal only which detained the water of crystallization. In many cases such as that of ammonia dissolved in water, where ammonia as such was also present, the hydrate theory could not be adopted as it stood. There was, in fact, no single theory at present able to explain all the phenomena observed.

Mr. Caldwell criticised the various methods used for measuring hydration. In the experiments of Jones, for example, whose method was open to objection, many of the results did not follow what would be expected from the law of mass action. Philip assumed that the dissolution of a gas was mechanical and that of a salt chemical. If that were true, a gas of small molecular weight, such as helium, should be really soluble.

Mr. W. A. Davis said that there were many cases of solution —e. g., in dyeing—which were covered by neither the ionic nor the hydration theory, but in which the process was purely mechanical.

Mr. Fenton said that it was not always very clear what was meant by hydrate. The methods hitherto employed for studying hydrates were chiefly physical, and the results obtained were capable of many interpretations. The problem should be studied in such a way that specific chemical properties were obtained.

In reply to Dr. H. Borns, Dr. Lowry said he imagined ionization to be the result of the separate hydration of the ionic constituents of the molecule.

The chairman (Prof. Pickering) thought that the agreement between the heat of formation of a salt in dilute solution and the sum of the separate heats of formation of the ions shown to exist by Mr. Bousfield and Dr. Lowry proved nothing, as the proof involved reasoning in a circle.

In reply, the authors explained that the agreement proved these properties of the ions to be additive, and so gave further support to the dissociation hypothesis.

London, Aug. 3, 1907.

MARKET REPORT FOR JULY.

Chemicals have still a downward tendency. Copper sulphate has dropped to £31 from £32 at the end of June. Ammonia sulphate is quoted £11.17.6, as against £12.10. Montreal potash is at £40 per ton. Bleaching powder 2s. 6d. lower at £4.10, and caustic soda (77 per cent) unchanged at £10.12.6. Zinc sulphate steady at £8. Copper has continued falling throughout the month. The end of June saw the price at £96.10, the 15th July showed £94.10, and the 29th £90. Three months' deliveries could be had at £86 at the month end, and the price has since weakened further. Tin continued to rise until the commencement of the second week in July, when £200 per ton was again paid. Fresh supplies dropped the price to £186 by the 15th. The market remained quiet during the closing week, £184 being the closing price.

Lead has receded to £20.16. Cleveland pig shows firmer at 57s. Hematites has risen to 78s. Antimony is quoted £43 to £45, a decided falling off.

Calcium Cyanamide Industry.—From the London *Electrical Review* of July 19 we gather the following notes on new calcium cyanamide plants in Europe. The Brandenburgische Carbidwerk G. m. b. H. has obtained a license for Germany and Norway, and is able to make about 2,500 tons per annum at its factory in Mühlthal (Bromberg), handing 5 per cent of the net profit to the Roman Co., which is the holding company of the cyanamide patents. A works is being built at Odde, in Norway, near the Alby United Carbide Factories, where some 12,500 tons of calcium cyanamide are to be made from 10,000 tons of calcium carbide, the latter being procured from the Alby factories. The Soc. Italiana Prodotti Azotati has obtained a license for Austria-Hungary, and is about to erect a second works, while the factory of the Societa per l'Utilizzazione delle forze Idrauliche della Dalmazia, which is already in existence there, has an annual capacity of about 10,000 tons. We have already noted that in this country the American Cyanamid Co. intends to erect a plant with an initial capacity of 20,000 tons per year at Muscle Shoals on the Tennessee River, in Northern Alabama. The trade name for calcium cyanamide will be lime nitrogen, which is the literal translation of the German Kalkstickotoff.

SYNOPSIS OF PERIODICAL LITERATURE

A Summary of Articles Appearing in American and Foreign Periodicals,

INDUSTRIAL ELECTROCHEMISTRY.

Electrolytic Rectifier.—The property of an aluminium electrode to permit an electric current to pass in one direction but not in the other direction has been used for the construction of electrolytic rectifiers and condensers, as has been repeatedly described and noticed in this journal. G. Schultze in a paper published in *Ann. d. Phys.*, No. 7, and abstracted in London *Electrical Engineering*, July 18, has found that tantalum is even superior to aluminium for electrolytic valve effects. There is no electrolyte in which tantalum fails to show a valve effect. The voltage which the non-conducting layer deposited on the anode is capable of resisting is also much higher, being over 650 in carbonate of soda, 600 in various fluorides, and 70 in concentrated caustic potash. It is best to have the tantalum electrode entirely immersed, as otherwise sparks may pass from the surface of the liquid to the emergent portion. Such sparks show the tantalum spectrum, whereas sparks through the liquid show nothing but the spectrum of the electrolyte. The anode skin is easily formed in the course of a few minutes, and is not much affected by heat. Herein it has a great advantage over aluminium. But this is to some extent balanced by the instability of the skin on tantalum electrodes, which is greatly reduced in efficiency in the course of a few minutes' break of the current. Niobium and vanadium also show a valve effect in all electrolytes, though it does not approach 1,000 volts, as in tantalum. Other metals, like Cu in copper sulphate, show a slight action of this kind, but it is not of any practical utility.

Electrolytic Lightning Arrester.—While the electrolytic rectifier has one aluminium electrode, the electrolytic condenser has two aluminium electrodes. As long as the voltage is below the critical valve, neither a direct current nor an alternating current is able to pass. For this reason the electrolytic condenser is very suitable as a lightning arrester. To use it on circuits of 4,000 to 60,000 volts, it is of course necessary to use a number of such cells in series. R. P. Jackson, in the August issue of *The Electric Journal*, describes how this is done by assembling them in tray form so that one may rest within another, insulated from each other, but all containing the electrolyte.. The electrolytic ligtning arrester is preferably used in conjunction with a horn ligtning arrester.

Calcium Nitrate as Fertilizer.—Calcium nitrate is the form of artificial fertilizer produced from nitric acid at the works using the Birkeland-Eyde process in Norway. An improvement mentioned in London *Electrical Review*, Aug. 9, due to E. Kollett and the Det. Norske Akt. for Elektrokemisk Industri of Kristiania, has the advantage that their new fertilizing product contains more nitrogen and is not hygroscopic. The calcium nitrate is mixed with a proper quantity, *i. e.*, about 40 per cent of ammonium sulphate, by mixing them together either in the state of powder or by melting the calcium nitrate. The product is a double salt, or a mixture of calcium sulphate and ammonium nitrate, which is stated to have the properties above mentioned. If the original calcium nitrate contains an excess of any base, it is advisable to add a corresponding quantity of superphosphate, or some other material having an acid reaction.

Tin.—In *L'Eclairage Electrique* of July 20, J. Reyval describes an electrolytic process for recovering tin which is stated to be in commercial use, the French patent being No. 364,589, of March 26, 1906. The tin is obtained not in spongy form but in thick plates from scrap of tin, scrap of tinned iron plates, etc. In the installation in which the process is in use, it is, however, applied to the treatment of the slimes which re-

sult from the winning of copper from copper-tin bronze by treatment with sulphuric acid. But it is stated that the process is equally applicable to natural ores after they have undergone an oxidizing roast and leaching. When slimes resulting from bronze are treated almost the whole tin is in the form of stannous hydrate which is to be changed into stannic hydrate; this offers no difficulties.

The first step of the process is the production of a solution of sodium stannate. The tin hydroxide is treated at boiling point with a caustic soda lye of 10 or 12 per cent in iron receptacles. A liter of a 12 per cent caustic soda solution dissolves 45 to 50 grams of tin. At the beginning of operation a freshly-made-up caustic soda solution is used, but later on the solution which has already been subjected to electrolysis and which contains a certain amount of sodium stannate is utilized, the necessary amount of stannic hydrate being added. If the process is not to be applied to the hydroxides of tin but to oxides, etc., the formation of the stannate is more difficult, although it can be facilitated by the addition of sodium nitrate.

The second step of the process is the purification of the sodium stannate solution. Copper and lead are the most dangerous impurities. For purification a very concentrated solution of sodium sulphide is employed at a temperature of 70 degrees C. Rapid stirring is necessary.

The third step consists of the electrolysis of the sodium stannate. This is carried out in iron receptacles with iron anodes at a temperature of 90 degrees C. The voltage is 2.4 and the cathodic current density 300 to 400 amperes per square meter, one single face of the cathode being counted. The cathodes may consist of tin foil or of tinned iron sheets. It is easy to connect 30 cells in series. Insulation difficulties arise when the total voltage is beyond 80. It is of greatest importance that the temperature should never fall below 80 degrees C.; that excessive current density should be avoided; that the electrolyte should contain sufficient sodium stannate; that the electrolyte should be strongly stirred or circulated, and that insoluble anodes are employed. The solution should always contain not less than 10 grams of tin per liter in order to get good deposits. To make up for evaporation, water is added from time to time. The deposit obtained by this process is stated to be excellent. The amount of tin obtained in practice per ampere hour is 0.8 gram when the current density is not too high. The electrolytic reaction is given in the form $SnO_2Na_2 = Sn + Na_2O_2$. At the anode the anions Na_2O_2, in presence of water give sodium hydroxide and oxygen according to the equation $Na_2O_2 + H_2O = 2(NaOH) + 2O$. If the electrolyte gets poor in sodium stannate it becomes rich in sodium hydroxide and then the electrolysis yields practically oxygen at the anode and hydrogen at the cathode. For this reason it is necessary to keep the strength of the electrolyte at the proper figure.

Manufacture of Chlorates.—In *L'Eclairage Electrique*, of July 27, G. Rosset begins what promises to become a long article on the manufacture of chlorates. He first gives an historical review of the manufacture of matches and an outline of processes for making chlorates from chlorine and caustic as starting materials which may or may not have been made electrolytically. He then gives a summary of the physical and chemical properties of potassium chlorate, sodium chlorate and barium chlorate.

Induction Furnace.—In London *Electrical Engineering*, July 18, we notice a patent of de Ferranti for induction furnaces in which the primaries consist of water-cooled tubes and means are provided for preventing the iron cores from reaching a temperature above that of maximum permeability. The new features appear to be that a rotary field may be arranged to circulate or mix the molten metal and that "the whole furnace is lagged with molded quartz."

Iron in the Electric Furnace.—The London *Electrical Review* of July 19 gives the following note on experiments car-

ried out recently by A. Hiorth in the new electrochemical institute of the Technical High School at Christiania. They are said to have shown that a good quality of metal can be obtained by electrically smelting a low grade of iron ore, unfit for reduction in the blast furnace, together with impure Norwegian graphite. The original iron-sand contains about 13 per cent of titanic acid and 20 per cent of silica, whereas the finished metal contains not a trace of titanium and only 0.01 per cent of silica. The graphite employed occurs in many parts of Norway in beds 30 to 60 feet thick.

Porous Diaphragms of Wood.—In London *Electrical Review* of July 19 it is stated that Q. Marino and E. W. Barton-Wright have taken out a French patent for a process to convert wood into a porous diaphragm fit for employment in electrolytic cells, and one which confers upon the material a high resistance to the corroding action of electrolytes. The process consists in treating wood for 8 to 10 hours with cuprammonium oxide, then removing the copper by treatment with 0.88 ammonia for 5 or 6 hours, next washing the wood and soaking it in crude nitric acid for from 2 to 4 hours (which converts the gummy material into a yellow resin) and finally exposing it to a blast of steam and sulphur dioxide for 5 to 15 minutes. The last operation results in the formation of a mixture of nitric and sulphuric acid, which converts the cellulose into nitro-cellulose and allows the latter to be dissolved out of the material with the aid of alcoholic caustic potash and ethyl acetate. The product is stated to possess a considerable amount of malleability.

LEAD.

The Roast-Reaction Process.—R. Schenck and W. Rassbach give in *Metallurgie* for July 8 a splendid study of the reactions of this process, undertaken experimentally with the guidance of the phase rule. The well-known reactions are formulated as:

$$PbS + PbSO_4 = 2Pb + 2SO_2.$$
$$PbS + 2PbO = 3Pb + SO_2.$$
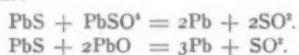
In the Huntington-Heberlein process the following reaction has been brought into use:

$$PbS + 3PbSO_4 = 4PbO + 4SO_2.$$

To complete the study, it is seen by applying the principles of the phase rule that one other reaction should be investigated, viz.:

$$PbS + PbSO_4 = 2PbO + SO_2.$$

These four reactions contain all possible chemical changes of these substances.

The first reaction given above was found to be reversible and to lead to an equilibrium; the following being the reaction tensions of the SO_2:

600° C.	30 m.m. Hg.
650° C.	143 " "
700° C.	442 " "
725° C.	735 " "

The activity of the reaction varies very considerably in a small range of temperature, and at any temperature within this range is dominated very strongly by the partial pressure of the SO_2.

The second reaction was also found reversible with equilibrium under the following conditions of SO_2 tension:

700° C.	10 m.m. Hg.
750° C.	35 " "
800° C.	99 " "
825° C.	286 " "
850° C.	550 " "
875° C.	850 " "

This second reaction takes practically 150° higher temperature to make it go than the first. At 800° PbS showed signs of volatilizing, and at higher temperatures vaporized rapidly. Also, the metallic lead formed in these reactions can dissolve

PbS in the melted state, and this solubility interferes or disturbs the normal course of the reactions to some extent.

The third reaction possesses no equilibrium temperature up to pressures of SO_2 of one atmosphere; it is possible, however, that such occurs for higher pressures. As it is, from 550° on the reaction proceeds irreversibly. The same is true of the fourth reaction.

In roasting PbS the concentration of the SO_2 has a great influence on the product; from 600° and pressure of 30 m.m. to 720° and pressure of 760 m.m., $PbSO_4$ tends to form; at lower tensions of SO_2 at these temperatures PbO forms; from 700° at tensions of SO_2 below 100 m.m. Pb forms, and above 880° Pb forms with any tensions of SO_2. The investigation throws much needed light upon the oldest and most-used reactions in the metallurgy of lead.

IRON AND STEEL.

Basic Bessemer Converters.—M. Belman has made some observations on the rate of cooling of the interior of a basic converter which may give some idea of the radiation losses during the Bessemer blow. He found the temperature of the lining at the hottest visible point as follows:

On stopping the blast	1,550° C.
One minute later	1,450° C.
Converter empty	1,350° C.
5 minutes after emptying	1,250° C.
10 minutes after emptying	1,200° C.
20 minutes after emptying	1,150° C.
35 minutes after emptying	1,100° C.

The observations would have been much more complete and serviceable if the temperatures of the outside shell had also been found, the temperature and velocity of the surrounding air, the approximate weight and constitution of the converter, so as to allow of calculating the actual heat units lost by the cooling. (*Revue de Metallurgie*, July.)

Steel Works Machinery.—We cannot do less than recommend most strongly to all our readers interested in handling heavy weights, fluid metal, charging furnaces and casting ingots, the perusal of Dr. G. Stauber's fine monograph of 85 pages, illustrated by 153 cuts, in *Stahl und Eisen* for July 10. It is a complete presentation of the most recent information on this subject.

COKE.

Coking of Coals.—In his presidential address before the Coal Mining Institute of America, F. C. Keighley discussed the question why some coals coke and others do not. The finest coking coals are of the bituminous class and their structure is such that upon fracture they exhibit a fingery or prismatic form and separate vertically, while the coals more difficult to coke and the ones of a bituminous character that cannot be coked at all are of a laminated structure and upon fracture break into cubical form, with a tendency to separate horizontally instead of vertically. This would indicate that the coking property depends very largely upon the "arrangement of the atoms or molecules composing the coal seam. If these atoms lie in the seam with their longer axis horizontal to the bedding of the seam, they are unfavorable to the coking process. On the other hand, if they are perpendicular to the strike of the seam, i. e., at right angles with its bedding, the coking tendency is much pronounced. It is likely that in all seams the longer axes of the atoms are lying at angles to the horizontal or the vertical. This would explain some of the mystery." Coke is being made to-day from coal that ten years ago was rejected as worthless for the purpose. Many people were attracted to such coals by the similarity of their chemical constituents to the Connellsville coking coal; yet while they would coke, the coke was unsuitable for the requirements of the consumer. Some of these coals were laminated in structure and others tended to the crystalline, and it has been

proved now that all that was required to make many of these condensed coals produce a fine grade of coking coal was simply to break them up to a greater or less degree of fineness and destroy, at is were, the natural polarity of the atoms making up the coal seam. This was accomplished in various ways, namely, by crushing, disintegrating and pulverizing. It is evident, then, that the coking principle of coal is dependent to an important extent on its structure. In the author's conclusions it is said that the reason for some coals coking or submitting themselves naturally and readily to the coking process and furnishing a high grade coke are as follows:

1. They are in structure largely prismoidal, permitting the free mixing of the particles, diffusion of gases, etc.

2. Their chemical composition is such that they contain not only the fusing and cementing factors in the most favorable proportions, but they carry the most desirable elements in those proportions and the form best adapted to the purpose for which the coke is required.

The reason some coals are not naturally fitted for the coking process, but yield high-grade coke after disintegration, are as follows:

1. Their structure is largely of a laminated character, thus presenting obstacles to the free mixing of the particles and diffusion of gases.

2. Their chemical composition is not widely different from those of the natural coking coals, but they cannot adjust themselves to the necessary processes of fusion, cementation and interchange of position of the different elements the complete coking process requires, unless the coal has first been disintegrated or pulverized.

ANALYSIS OF CURRENT ELECTRO CHEMICAL PATENTS.

ELECTRIC FURNACES.

Reduction of Oxide Ores in Electric Furnace.—A. J. Petersson, 858,621 and 858,622, July 2, 1907. Application filed Oct. 30, 1906.

The principal object of these two patents and of the one analyzed in the next abstract is to utilize to the fullest extent the calorific value of the fuel in the furnace. Fig. 1 shows a vertical and a horizontal section of the electric furnace. There are three shafts, 1, 2 and 3, of which 1 and 3 are charged with ore and 2 with coal, anthracite, etc., or the like. The lower parts of the shafts are in open communication with each other, but, nevertheless, the carbon and the ore also here form separate layers or columns, the columns of ore closely surrounding the column of carbon. The carbon column constitutes the reduction and melting zone proper. Current is introduced into the furnace through the electrodes 7, 8, which are in contact with the carbon column in the furnace. When the furnace has been charged about to the height indicated in the upper diagram, the lower part of the carbon is heated to incandescence by turning the current on. The ventilator 21 is then put in operation, and a current of air is circulated in the direction of the arrow. When the air passes through the column of incandescent carbon it is burned to CO and at the same time intensely heated. In then passing through the column of ore below shaft 1, this ore is reduced by the CO with production of CO_2. The mixture of CO_2 and air then passes through the channels 16 into the regenerator 18, where it gives off its heat. The gas mixture then passes through the pipe 20 and the ventilator 21 in a comparatively cold condition, whereby losses of heat and injuries on the ventilator are obviated. The gases then again enter the system, and this circulation is carried out continually, the result being that the gas is successively converted into CO within the carbon of the charge and reoxidized to CO_2 by the ore. The excess of gas flows off through the shafts 1 and 3 and the outlets 22 and 23. Simultaneously, heat

is transferred by the circulating gas to the column of ore below the shaft 1 and to the regenerator 18, which absorbs the remaining heat of the gas. By this transfer of heat and by direct conduction of heat the reduced metal melts and drops down into the reservoir 9. In order to keep it molten this reservoir is carried out in form of an annular trough, which is heated on the principle of an induction furnace, a transformer core 15 with a suitable primary coil 14 being provided for this purpose.

When the desired quantity of heat has been stored up in the regenerator 18 the ventilator is reversed so that the gas
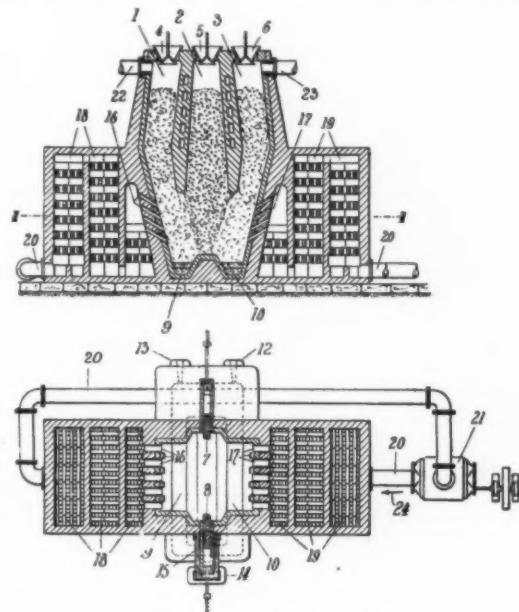
FIG. 1.—ELECTRIC FURNACE.

will circulate in opposite direction. The regenerator 18 is now cooling down and the regenerator 19 is heating up. When this has been done to a sufficient degree the direction of the circulation of the gases is again reversed and this reversal is repeated as often as suitable. Eventually the direction of the reversal of the flow of the gases may be made at so short intervals that the mass of gas partaking in the reaction will oscillate in the column of carbon and the column of ore on each side thereof. The central column of carbon, which is electrically heated, reduces the CO_2 formed in the reduction of the ore, and thus yields new CO for reducing the column of ore on the other side. The object of the regenerators is to prevent losses of heat otherwise caused by the heat being moved by means of the circulating gases.

When volatile ores such as zinc are to be reduced a column of carbon may suitably be arranged on each side of the column of ore. The mixture of metal vapor and carbonic acid formed in the reduction of the ore will then always—independently of the direction of circulation—pass through a column of carbon heated to incandescence, so that the CO_2 is fully reduced to CO, and no CO_2 is mixed with the zinc vapor which could oxidize it again.

In 858,622 the same process is described, but emphasis is laid on the fact that the excess of carbonic oxide formed in the reduction process is utilized for the preliminary heating of the charge.

Calcium Carbide Process.—A. J. Petersson, 858,623, July 2, 1907. Application filed Oct. 13, 1906.

The principle is the same as that described in the preceding abstract. Fig. 2 shows an electric furnace specially adapted for the manufacture of calcium carbide; 1 and 2 are the two

electrodes. The carbon is introduced so as to form a column around the two electrodes, while the lime is introduced at both sides of the carbon column, so as to fill the space between the latter and the walls of the furnace. The current passes mainly through the carbon column


FIG. 2.—CARBIDE FURNACE.

and heats it so as to cause its reaction with lime at the contact surface, thereby forming CO gas and calcium carbide, which melts and accumulates at the bottom of the furnace. Air is drawn through the suction fan 6 so as to pass through the charge downwards and through holes in the walls into the annular channel 3. When the air comes in contact with the CO gases the latter burn and develop an intense heat in the outer part of the lime layers, which are thus intensely preheated before entering the reaction zones of the furnace.

Calcium Carbide Furnace.—A. J. Petersson, 863,044. Aug. 13, 1907. Application filed Oct. 30, 1906.

While the usual practice in the manufacture of calcium carbide is to charge into the electric furnace a mixture of crushed lime and carbon, this has the disadvantage that those particles of lime which come into contact with the carbon electrodes enter into chemical reaction with the latter so that the electrodes furnish carbon for the production of calcium carbide. This is not desirable, since the electrodes are far more expensive than the carbon in the charge. The present inventor proposes to charge the lime and carbon separately in such a way that the carbon alone comes in contact with the electrode. The current then passes principally through the carbon layer, and since the arrangement may be made that the charge of carbon is in the center of the furnace good heat insulation is provided. The layer of lime in contact with the carbon is reduced, forming carbonic oxide, which passes off, and calcium carbide, which melts and may be drawn off at suitable intervals.

Joint for Carbon Electrodes.—F. J. Tone, 863,674, Aug. 20, 1907. Application filed Sept. 25, 1906.

Since graphite electrodes have come into use for electric furnaces it has become customary when it is desired to assemble two or more pieces to thread one piece into another. In this way a new electrode can be joined to the end of one in use, and thus electrodes can be fed into the furnace one after another without interruption. In order to produce a joint of high conductivity and good mechanical strength the inventor uses a tapered threaded joint such as shown in Fig. 3, where 2 and 3 are the carbon electrode pieces to be joined. The ends of the two pieces are provided with a tapered threaded portion and a tapered threaded socket, respectively.

Manufacture of Phosphorus in the Electric Furnace.—G. C. Landis, 859,086, July 2, 1907. Application filed April 9, 1907. Assigned to American Phosphorus Co.

If the charge of a phosphorus furnace is reduced to a finer powder than is usual at present the temperature in an electric phosphorus furnace, which is said to be now about 3,500° F., may be reduced to 2,700°, which is an advantage for the con-

FIG. 3.—JOINT FOR ELECTRODES.

densing of the phosphorus. However, if the charge consists of a very fine powder a great percentage of the dust is carried over unreduced into the condenser. This is avoided by the present inventor by briqueting the very finely divided charge before treating it in the furnace. The ingredients, such as phosphates, sand, silicate and coke are crushed, one independently of the other, and each calcined at a red heat, preferably in a rotary calcining furnace, then each ingredient is ground to about 18-mesh and the proper mixture is prepared in form of briquets. If a bond is used containing water the briquets are thoroughly dried before being put into the electric furnace. The briquets may, however, be mixed dry with a suitable bond or a bond of tar may be used.

Low-Carbon Ferro-Alloys.—E. F. Price, 862,996, Aug. 13, 1907. Application filed Nov. 14, 1905.

To produce ferro-alloys, low in carbon, by a continuous operation, the inventor uses a process in two steps. In the first step ferro-silicon, high in silicon and low in carbon, is produced by electrically smelting a charge of silica, iron ore or iron and carbon in an arc furnace. The molten silicide is then tapped from the smelting furnace and percolated through a granular body of the compound to be reduced, for instance, chromite. The silicon effects the reduction of the oxides of chromium and iron in the charge and the reduced metals alloy with the percolating iron. A basic flux, such as lime, is preferably mixed with the chromite to convert the silica produced by the reduction of oxide ores into a fusible slag. The granular mixture of chromite or other ore and lime is preferably heated by interposing the mixture as a resistance-conductor in an electric circuit, both the heated charge and the percolating metal serving to carry the electric current.

Electric Smelting of Iron Fines.—H. W. Lash, 862,978, Aug. 13, 1907. Application filed Dec. 20, 1905.

This is another patent referring to his process which was already described in our July issue, page 279, and August issue, page 322. The charge consists of iron sand or scale, finely divided cast or pig iron, coke, sawdust and fluxes, such as lime or fluorspar. A content of titanium in the iron oxide is not troublesome. The present patent refers to the proportions of
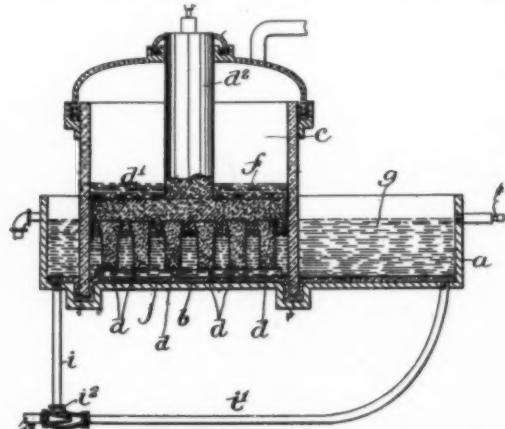

FIG. 4.—MERCURY CATHODE CELL.

the different ingredients in the mixture, and as suitable examples the three mixtures are stated, the constitution of which was already given on page 322 of our August issue.

Mercury Cathode Cell.—E. A. Allen, 862,783, Aug. 6, 1907. Application filed July 17, 1905. Assigned to Allen Electrochemical Co., of Rumford Falls, Me.

The sodium chloride solution f is electrolyzed in the receptacle c with a carbon anode consisting of blocks or bars d, which are dovetailed into the support d^1 and rest upon longi-

tudinal glass bars *j*. Mercury *b* in the bottom of the vessel forms the cathode. Through the mercury this inner vessel *c* is in connection with an outer vessel *a* in which caustic soda is made when the sodium amalgam formed in the inner vessel is brought to the outer vessel into contact with water. This circulation of the mercury is brought about by the pipe *i*, which contains a T-coupling *i*². The T-coupling contains an injector so that steam introduced into the pipe *i*³ forces the mercury or the amalgam to flow in the direction of the arrow. The introduction of the steam not only serves to effect the circulation, but also breaks up the amalgam largely in the pipe *i*¹ itself, but this reaction still continues when the amalgam reaches the water *g* in the outer tank.

Electroplating Metal Sheets.—J. Müller, 862,409, Aug. 6, 1907. Application filed April 18, 1906.

In order to coat sheets or plates by electrolysis in a continuous manner the edges of the sheets or plates are connected temporarily together so as to form a long, continuous band, and this band is then passed through the electrolyte.

Treatment of Albuminous Substances.—R. Desgeorge, 863,-268, Aug. 13. 1906. Application filed Nov. 2. 1906.

The object is the treatment of certain substances having an albuminous base, for instance, casein, for obtaining non-inflammable products in imitation of horn, shell, ivory, celluloid, etc. The casein is diluted with a solution of chloride of sodium and electrolyzed between metal electrodes. If copper electrodes are used the casein assumes a clear green color after the passage of the current for some moments, owing to its reaction with copper oxide, and if the operation is prolonged the green color will become darker and darker owing to the greater absorption of oxide of copper, and the compound will become completely insoluble. If lead or aluminium electrodes are used the casein will combine with the oxide of the respective metal and become insoluble, but it will not assume any color. In this case it may be colored by aniline dyes if desired. The substance thus obtained either alone or mixed with other substances is treated to reduce it to the desired form, and may then be subjected to the action of the vapors of reducing bodies, such as formic acid, formaldehyde or solutions of such bodies.

Storage Battery.—C. Berst, 863,347, Aug. 13, 1907. Application filed April 16, 1906. Assigned to Gamewell Fire Alarm Telegraph Co.

Details of construction to prevent the escape of gases and the bubbling over of the liquid during charging. The cover of the battery is so formed as to provide a large extent of cooling surface to guide the condensed liquid back to the battery container. For this purpose the top of the battery has a "flange resting upon and projecting beyond the upper edges of the cell, the top being provided with a depending flange having concave curved sides and ends terminating in an edge extending in the direction of the length of the top."

RECENT METALLURGICAL PATENTS

IRON AND STEEL.

Composition of Steel.—J. W. Spencer (863,763, Aug. 20, 1907) patents a composition of steel which is stated to be specially suitable for boiler plates, ship plates and all classes of forgings such as are made from so-called mild and medium hard steel. For this purpose he adds to all kinds of mild and medium hard steels containing carbon from 0.05 up to 0.25 per cent, a larger proportion of silicon than is now used commercially for such purposes, namely, from 0.75 to 2 per cent of silicon.

Agglomerating Pulverulent Iron Ores.—In order to agglomerate magnetic concentrates or blast-furnace dust, etc., W. Schumacher (862,666, Aug. 6, 1907) briquets them with colloidal calcium silicate as a binding medium. Very finely

ground quartz or flint (the finer and purer the better) is mixed with pure finely ground oxide of lime or hydrate of lime, preferably in equal parts. With this compound is then mixed, together with addition of the necessary amount of moisture, the dust or powder to be agglomerated, an admixture of about 5 per cent of the quartz-lime compound being generally sufficient. The briquets are hardened by subjecting them to the action of steam under pressure in a closed vessel.

ZINC.

Treatment of Sulphide Ores.—R. W. E. MacIvor (863,411, Aug. 13, 1907. Assigned to Metals Extraction Corporation, Ltd.) proposes the following treatment of sulphide ores containing zinc. The ore is first slowly roasted to a dull red heat under conditions which are favorable to the conversion of as much as possible of the zinc in the ore into soluble sulphate of zinc, leaving the remainder of the zinc in the ore as oxide of zinc. The roasted ore is then leached with boiling water to dissolve all the zinc sulphate, and this solution after settling is run off into tanks, where it is mixed with a solution of calcium chloride when calcium sulphate is produced and precipitated, and at the same time the chloride of zinc formed passes into solution. The latter is run off from the precipitate and is the special means for dissolving out the zinc oxide in the leached ore. For this purpose the ore is digested in the solution of zinc chloride at boiling point, whereby the chloride of zinc in solution becomes an oxychloride, approximately $ZnCl_2, 3ZnO$. To this solution is added either slaked lime, carbonate of lime, magnesia or soda ash in sufficient quantity to completely decompose the zinc chloride. The precipitate of hydrate or carbonate of zinc is finally washed free from chloride. The ore after removal of the zinc content is treated for lead, silver, copper by the usual smelting process.

TIN.

Detinning.—Another patent (862,860, Aug. 6, 1907) has been granted to Mr. C. E. Acker for the detinning of tin scrap. In the present case the scrap is partially submerged in an anhydrous liquid capable of directly dissolving or reacting on the tin and of evolving a vapor or gas which will react on the unsubmerged portions of the scrap. Liquid reagents which may be employed are solutions of chlorine or bromine in carbon tetrachloride or stannic chloride, or a solution of anhydrous hydrogen chloride in benzol or toluol. The solution is heated to furnish an atmosphere containing a considerable percentage of chlorine or bromine or hydrogen chloride. In some cases an additional supply of chlorine may be pumped into the receptacle during treatment.

ALUMINIUM.

Solder.—C. Ellis (863,058, Aug. 13, 1907) patents a solder for aluminium which consists of "tin 30 parts, zinc 7 parts, aluminium ¾ part, manganese 1/10 part; or using chromium with manganese, tin 30 parts, zinc 8 parts, aluminium 1 part, manganese q. s., chromium 1/16 part."

VANADIUM.

Leaching Process.—F. de Lucio (863,076, Aug. 13, 1907) proposes the following process of treating vanadium ores. Oxidized ores (or roasted sulphureted ores) are first boiled with a solution of hypochlorite of sodium, containing more than six atoms of sodium to one molecule of vanadic acid in the ore. This will oxidize all the vanadium to pentoxid, chlorine will be evolved, and the resulting vanadate of sodium is then dissolved as such and extracted with hot water. The solution of alkaline vanadate, when cold. is treated with a like amount of hypochlorite of calcium. Vanadate of calcium is precipitated and hypochlorite of sodium regenerated, which latter can be used again for the treatment of new ores, increasing its content of alkaline hypochlorite to the required amount. The process therefore consumes only hypochlorite of calcium and steam.

ALLOYS.

Substitute for Bronze.—W. Ruebel (864,139, Aug. 20, 1907) produces an alloy composed in accordance with the formula (CuFe)₂NiAl. When 6 parts of this alloy are mixed and fused together with 54 parts of copper and 40 parts of zinc, the product is stated to cost about 1 mark (25 cents) per kw., and to equal in strength, hardness and resistance the best bronzes hitherto produced. It is, therefore, claimed to be suitable for replacing such bronzes. Rules are given concerning the procedure of repairing the alloy.

Bronze.—The same inventor (864,140, Aug. 20, 1907) patents an "atomic-weight alloy" of zinc, aluminium, silicon, copper, consisting of 65.4 parts of zinc, 27.1 aluminium, 28.4 silicon and 63.6 copper. If this alloy be added to alloys of copper and aluminium by taking, for instance, 8 kg. of copper, 769.2 aluminium and 238 grams of the above alloy, a bronze is said to be produced having 99.2 kg. tensile strength, which is hard steel, but, nevertheless, readily adapted for forging and rolling. If in the above alloy silicon is omitted and pure nickel is substituted, so that the alloy contains 63.12 copper, 64.91 zinc, 26.91 aluminium and 58.3 nickel, the resulting bronze retains the strength of about 100 kg. per square mm., but the hardness has still further increased. The property of being readily forgible is not lost. These bronzes are said to be very resistive against chemical influences and to be particularly well adapted for shipbuilding purposes and for gun barrels. The limit of elasticity lies only 12 per cent below the rupture strength.

MISCELLANEOUS.

Pebble Mills.—A patent granted to Max L. Abbe (858,129, May 25, 1907) relates to a lining for pebble mills. The cylindrical mill is provided with a number of natural lining stones, each embedded at the sides, ends and back in a coat of hardened cement.

Speed Recorder.

The importance of keeping a continuous record of the speed of blast-furnace blowing engines on a chart has been the incentive for Messrs. Edward Brown & Son, 311 Walnut Street, Philadelphia, to devise a new recording revolution indicator. How well the instrument is adapted for this purpose is shown by the adjoining illustrations.

Fig. 1 is a photograph of a chart taken from a Brown recording revolution indicator in use on a blowing-engine at an Eastern Pennsylvania furnace. It will be noted that the number of revolutions per minute fluctuates several revolutions at

Fig. 3 is a reproduction of a chart taken from one of these instruments in use on a gas blowing-engine of a well-known type at the Park Gate Iron & Steel Co., Rotherham, England. It is evident that with the use of a gas blowing-engine the number of revolutions of the engine is subject to very sudden and great fluctuations. This is a feature that must be of considerable importance in the operation of blast furnaces with gas blowing-engines, for, according to the record illustrated, a fluctuation of as much as 10 revolutions per minute occurs at intervals of every few minutes except for a space of several hours, during which time the speed did not vary a revolution. It is difficult to give a reason for such a peculiar record unless the conditions in England are greatly different from those in the United States.

Fig. 4 is a photographic reproduction of a chart used on the recording revolution indicator on a gas blowing engine at a well-known German works. It has been necessary to make some slight changes in the design of the instrument to suit the conditions in Germany, but this has not affected the successful use of the recorder.

The recording - revolution indicator itself, as illustrated in Fig. 5, is based on the law of centrifugal force, a body of mercury contained in a central chamber being thrown out into revolving arms proportional to the

FIG. 5.—SPEED RECORDER.

speed at which the instrument is driven. A float resting on the mercury is suitably connected to a pen arm which marks the record on the chart. These instruments have heretofore been furnished with a chart 6½ inches in diameter, but the inventors are now manufacturing the instrument with an 8-inch chart, affording wide graduations.

Although the recording-revolution indicator has heretofore
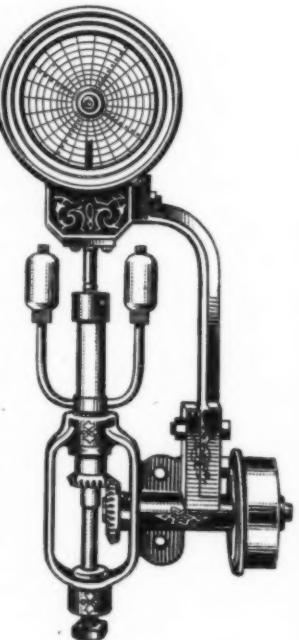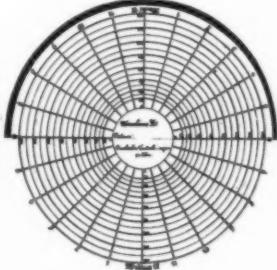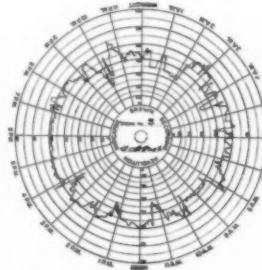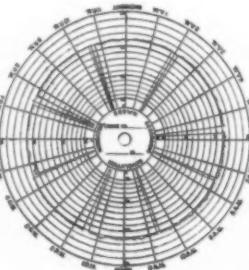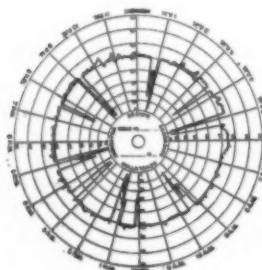
FIG. 1, 2, 3, 4.—SPEED RECORDER DIAGRAMS.

times. The hour or minute at which the engine has been slowed down or stopped is clearly shown.

Fig. 2 is a record made at the Youngstown Steel Co., Youngstown, Ohio, on a blast-furnace steam-blowing engine, and is a very fine chart, the number of revolutions having been kept within a quarter of a revolution except at stated intervals when the engine was stopped.

been chiefly used on blast-furnace engines, there is nothing to prevent its successful operation on all types of engines, machines, dynamos and motors where a record of the instantaneous speed is desirable. It becomes daily more evident that the best method of control over a large plant is with the aid of recording instruments, which give a true picture of all conditions of working at any moment.

New York Meeting of the American Electrochemical Society.

The Autumn meeting of the American Electrochemical Society, which is to be held in New York City, will probably not take place in the first or second week, as had been intended, but in the second half of the fourth week. The dates will probably be Oct. 24 to 26, but the matter is to be definitely settled at a meeting of the New York Section called for Sept. 7.

As far as the program has already been prepared it appears that there will be a great many interesting papers presented.

All the meetings will probably be held at the Chemists' Club, and the convention will be opened by an evening session on Thursday, Oct. 24, when Mr. E. G. Acheson will present an experimental lecture on deflocculated graphite and Dr. George F. Kunz will speak on moissanite. Other sessions devoted to the reading and discussion of papers will be held on Friday morning and Saturday morning, and probably on Friday night.

On the electrometallurgy of iron and steel papers are expected from Dr. Eugene Haanel, Dr. R. S. Hutton, Mr. Gustave Gin, and a joint paper by Messrs. A. E. Green and F. S. MacGregor.

Dr. Allerton S. Cushman is expected to present an experimental lecture on the corrosion of iron as an electrochemical phenomenon, and papers on the same subject, or at least discussions of it, are expected from Dr. W. R. Whitney, Dr. W. H. Walker and Mr. C. J. Reed.

On the electrometallurgy of zinc a paper is expected from Mr. Gustav Gin, while Mr. C. E. Baker will discuss the use of chlorine in metallurgy.

Other papers are expected from Mr. F. A. J. FitzGerald on heat conductivity of graphitized carbon, from Mr. A. B. Marvin on electrochemical patents, from Drs. Patten and Robinson on the electrolytic reduction of nitric acid, from Mr. W. R. Mott on over-voltage, from Prof. Carhart on calculations of e. m. f. of concentration cells, from Dr. Weedon on the titanium arc, from Mr. E. E. Free on the electrolytic determination of minute quantities of copper. Messrs. Fireman, Becket, Guess, Hambuechen and Schlundt are also expected to present papers.

The program of the excursions and social functions will be made up on Sept. 7 at the meeting of the New York Section, and the full program will then be issued as soon as possible. It is hoped that a visit can be arranged to Mr. T. A. Edison's laboratories.

Autumn Meeting of the Iron and Steel Institute.

The Autumn meeting of the Iron and Steel Institute (London) will be held in Vienna, Austria, on Sept. 23 and 24, in the building of the Austrian Engineers' and Architects Society.

The list of papers to be presented is as follows:

On the Development of the Iron Industry of Austria since 1882. By W. Kestranek.

On the Styrian Erzberg Iron Ore Mines. By Prof. H. Bauerman.

On Steel and Meteoric Iron. By Prof. F. Berwerth.

On the Determination of the Quantity of Blast Furnace Gas for a Given Make of Pig Iron. By Prof. Josef von Ehrenwerth.

On the Application of the Laws of Physical Chemistry to the Metallurgy of Iron. By Baron H. von Jüptner.

On Case Hardening of Mild Steel. By C. O. Bannister and J. W. Lambert.

On a New Blue-Black Paint as a Protective Covering for Iron. By F. J. R. Carulla.

On the Hardening of Steel. By L. Demozay.

On the Structure of Hardened Steel. By Percy Longmuir.

On Case Hardening. By G. Shaw Scott.

On the Ageing of Mild Steel; Further Notes. By C. E. Stromeyer.

On the Economical Distribution of Electric Power from Blast Furnaces. By B. H. Thwaite.

Notes.

Generators for Electrolytic Refineries.—Bulletin No. 83 of the Crocker-Wheeler Company, of Ampere, N. J., gives an illustrated description of generators for electrolytic purposes, especially for copper refineries. The voltage of the usual types varies from 80 to 125 (the proper number of electrolytic cells being connected in series to suit the voltage), while the current is generally several thousand amperes. One of the illustrations shows two 1,050-kw., 10,000-amp., 100-r. p. m. generators, which are part of the 3,370-kw. equipment of the Crocker-Wheeler generators in the plant of the United States Metals Refining Co., of Chrome, N. J. The special requirements of electrolytic generators are that the voltage shall be stable through a wide range of adjustment, and that the generators shall run continuously at their rated loads, where continuously means 24 hours a day every day in the year. In cases of leakage increased current density, etc., the generators have even to carry considerable overloads. The pamphlet gives notes on general design, construction of magnet frame, armature clearance, field coils, armature, commutator, brush rigging and mounting of armature.

Steam and Engineering Specialties.—The Schutte & Koerting Co., of Philadelphia, Pa., have just issued their export catalog for 1907 in the Spanish language, containing condensed illustrated descriptions of the many engineering specialties which they manufacture, such as steam jet exhausters and compressors, specialties for agitation of liquids and absorption of gases, lead exhausters and ventilators, valves, syphons, spray nozzles, sulphur furnace, etc.

The Colorado Iron Works Co. reports a very large business in smelting equipment during the past few months, the orders coming from all quarters. While the bulk of this business is from the United States and from Mexico, other foreign countries have been represented, and orders for either furnaces or complete smelting plants are now going through the shops for installation in France, Japan, Chile and New Zealand. The furnace included in the Chilean plant is designed for hot-blast smelting, and the New Zealand order embraces the complete equipment of a hot-blast copper matting plant with sampling plant.

The Denver Fire Clay Co., of Denver, Col., have sent us their illustrated catalog for 1907, which covers the following subjects: Chemists' and assayers' laboratory supplies, special chemical apparatus for analytical work, outfits for assayers and prospectors, school sets of chemical apparatus, collection of minerals, models and charts, fire-brick, tile and fire-clay material, chemicals and reagents.

Safe Blowing in Germany.—In the article by Mr. M. U. Schoop in our last issue (page 308) on a burner for cutting metals, he mentioned as a great disadvantage the possibility of opening by its means within a few minutes the largest "fireproof safe." This is illustrated by the story of a robbery carried out by a single, unaided man in Dresden. This story is told in a recent consular report as follows: "In a hotel a room was secured, which was situated immediately above the office of a money changer. At night a hole was pierced in the ceiling of this office. By the use of a drill and saw a circular piece of the flooring was easily raised. Beneath lay a thick layer of cement. A small orifice was made in this and an

umbrella shoved down into the space below. The umbrella was attached firmly from above, and when opened received without noise all the fragments of cement which were dislodged as the hole was enlarged so as to allow of the easy passage of a person. By means of a rope ladder the descent was readily made into the office below. Curtains were drawn, and with heavy blankets a tent was constructed around the safe, so thick that no ray of light could pass through. Next the robber brought down two cylinders of compressed oxygen and an acetylene generator charged with calcium carbide and water. With these he was able to produce a blow-pipe flame of such intensity that steel fuses in it like lead in an ordinary gas jet. It required but a brief space of time to melt away so much of the door that all the contents of the safe were accessible. They were carried to the room above. At an early hour the robber left his lodgings and disappeared without trace."

The Production of Fluorspar in 1906.—The three principal classes of consumers of fluorspar are, in order of importance, smelters and metallurgists, makers of opalescent glass and enamelled wares, and chemical manufacturers, the various uses of material depending on its chemical composition, its fluxing properties, its phosphorescence when heated, and its optical and gem-like properties. Chemically it is calcium fluoride, and consists of calcium and fluorine in the proportions of 51.1 to 48.9. The mineral is crystalline, only slightly harder than calcite, and crushes easily. In color it ranges, according to purity, from a clear, slightly bluish, glass-like substance through various brilliant shades, although much of it is white and opaque. The mineral is usually very pure, the material marketed running from 98 to 99 per cent of calcium fluoride, while material carrying less than 95 per cent finds little sale. Associated with other minerals, fluorspar has a broad distribution geographically and a wide range geologically. The deposits thus far exploited in the United States are, however, confined to five States—Arizona, Colorado, Illinois, Kentucky and Tennessee. The total production of marketed fluorspar in 1906 is reported by the United States Geological Survey in an advance chapter from *Mineral Resources of the United States, Calendar Year 1906*, at 40,796 short tons, valued at $244,025. These totals are less than those of 1905, which surpassed all previous records in quantity and average value per ton. The decrease in 1906 was perhaps due to over-production in 1905, resulting in surplus stocks which were sold in 1906, for at the close of 1906 the tendency of demand and prices was reported to be upward. Considerable fluorspar is imported at the present time, but the market is practically limited to the Atlantic Coast, as the cost of freight from English seaports to points west of New York tends to restrict the trade. English fluorspar has heretofore been cheap, at times selling at a price below the present cost of production, the shipments having been made from refuse dumps or abandoned lead mines, besides being brought to America as ballast, duty free. The local and the American demand will probably consume these English fluorspar mill-tailings within a few years, and thenceforth the material cannot be profitably exported to America, as the mines are closed. The chapter on fluorspar, with a few notes on cryolite production, was prepared by Ernest F. Burchard, of the survey, and includes a list of recent publications on the subject.

Obituary.

We record with regret the death of Sir William Perkin, which occurred on Sunday, July 14, at his residence at Sudbury, Middlesex, England. Sir William, who was best known as the founder of the coal-tar industry, was born in London in 1838, and received his technical education at the Royal College of Chemistry. While conducting researches on the possibility of artificially preparing quinine, he found the artificial dye-stuff mauve. This discovery and its adaptation led to the formation of the firm of Messrs. Perkin & Sons, and to the foundation of the aniline dye industry. Sir William Perkin's physical work chiefly consisted in researches on magnetic rotation for the results of which he was awarded the Davy and Longstaff medals. He was elected a Fellow of the Royal Society in 1886, and was awarded the Royal medal in 1879 and the Davy medal in 1889. He was president of the Chemical Society in 1883, and president of the Faraday Society during the present session. Sir William Perkin visited this country last year to attend the jubilee of the coal tar industry.

Digest of U. S. Patents.

Calcium Carbid (*Continued.*)

No. 588,012, Aug. 10, 1897, Isaiah L. Roberts, of Brooklyn, N. Y.

The apparatus is similar to that of the preceding patent, except that a reflecting dome of lime-brick or calcined limestone, enclosed in pulverized lime and brick work, is arranged over the arc to concentrate the heat upon the mixture below.

No. 598,592, Sept. 7, 1897, Sylvain Blum and Daniel J. Clark, of Galveston, Tex., and Sam Lazarus, of Sherman, Tex.

A charge for the production of calcium carbid, consisting of air-slaked lime, 22 bushels; pulverized carbon, 8 bushels; pulverized plumbago, containing iron, 4 bushels, and pulverized potash, ½ bushel. The ingredients are mixed and smelted by an arc. The iron associated with the plumbago and the "potash or carbonate of potassium" act as fluxes, while the carbid contains "a trace of potash."

No. 589,967, Sept. 14, 1897, Robert F. S. Heath, of Camden, N. J.

A charge for the production of calcium carbid containing a small amount of sodium carbid, consisting of quick-lime, 9 parts, and carbon, 4 parts, plus ¼ ounce of sodium or potassium chlorid to each pound of mixed lime and carbon. Limestone, chalk or oyster shells may be substituted for quick-lime. The carbon may be coke, coal or charcoal.

No. 590,057, Sept. 14, 1897, William Henry Fahrney, of Chicago, Ill.

A plastic charge to be calcined into cement, or one for the production of calcium carbid, is continuously formed into a tube which is fed into one end of a combustion furnace. The flame from the furnace passes around and through the tube. The tube may be heated electrically instead of by combustion, by passing it through and in contact with a tubular carbon electrode, and thence springing an arc to a cylindrical carbon electrode at the end of the first electrode. As the tubular charge is smelted the product falls away from the annular space between the electrodes. The hot gases pass upward through the tubular charge and dry and pre-heat it.

No. 590,514, Sept. 21, 1897, Alfred H. Cowles, of Cleveland, Ohio.

Downwardly-inclined carbon electrodes are buried in a charge of lime and coke. An arc is sprung between them and a pool of molten calcium carbid forms within the charge. The electrodes are gradually separated, and the current thereupon flows from one electrode to the pool of carbid and thence to the other electrode. The voltage may be from 40 to 70. The charge protects the electrodes from oxidation and acts as a heat insulator. Additional charge material is fed in from time to time and settles downward between the electrodes. A portion of the molten carbid may be tapped out by pushing a bar obliquely upward through a side hole in the furnace wall and through the charge to the pool. This hole is closed with a plug after tapping.

NEW BOOKS.

THE ELEMENTS OF CHEMICAL ENGINEERING.—By Dr. J. Grossman, with a preface by Sir William Ramsay. 152 pages, 50 illustrations. Bound in cloth. Price, $1.50. Philadelphia, Pa.: J. B. Lippincott Co.

A LABORATORY OUTLINE OF GENERAL CHEMISTRY.—By Alexander Smith. Third edition, revised in collaboration with W. J. Hale. 139 pages, illustrated. Bound in cloth. Price, 90 cents. New York: Century Co.

THE MINERAL INDUSTRY DURING 1906.—Its statistics, technology and trade. Vol. XV. Edited by Walter Renton Ingalls. 954 pages, illustrated. Bound in cloth. Price, $5. New York: Hill Publishing Co.

THE CORROSION OF IRON.—By Allerton S. Cushman. 35 pages, illustrated by diagrams. Bound in paper. Price, 15 cents. Washington, D. C.: Superintendent of Documents.

THE UNITED STATES STEEL CORPORATION.—A study of the growth and influence of combinations in the iron and steel industry. By Abraham Beiglund. 180 pages. Bound in cloth. Price, $1.50 net. New York: The Macmillan Co.

THE COPPER MINES OF THE WORLD.—A concise, geological and statistical study of the copper mines and deposits of all the world. By Walter Harvey Weed. 375 pages, 159 illustrations. Bound in cloth. Price, $4. New York: Hill Publishing Co.

ANNUAIRE UNIVERSEL DES MINES ET DE LA METALLURGIE.— By Robert Pitaval. (Large edition, comprising the whole world.) Price, francs 15. Paris: Société Anonyme des Publications Scientifiques et Industrielles.

PETIT ANNAIRE MINIER ET METALLURGIQUE.—By Robert Pitaval. (Small edition of the book mentioned before, relating to France and the French colonies only.) Price, francs 5. Paris: Société Anonyme des Publication Scientifiques.

UNITED STATES MINING LAWS AND REGULATIONS THEREUNDER—Approved May 21, 1907. 66 pages. Price, 15 cents, paper binding. Washington, D. C.: U. S. office of the Superintendent of Documents.

WILSON'S MINING LAWS.—United States, Arizona, California, Nevada and Utah, with forms and corporation laws of Arizona. Second edition revised. 132 pages. Bound in cloth. Price, $1; paper binding, 50 cents. Los Angeles, Cal.: Baumgardt Pub. Co.

CONCRETE STEEL BUILDINGS.—By W. Noble Twelvetrees. 420 pages, illustrated. Bound in cloth. Price, $3.25 net. New York: The Macmillan Co.

THE MECHANICAL ENGINEERS' REFERENCE BOOK.—A handbook of tables, formulas and methods for engineers, students and draftsmen. By Harrison Suplee. Third edition, revised and enlarged. 939 pages, illustrated. Bound in limp leather Price, $5 net; with thumb index, $5.50 net. Philadelphia, Pa.: J. B. Lippincott Co.

DIAGRAMS OF ELECTRICAL CONNECTIONS. By Cecil P. Poole. 113 pages; illustrated by diagrams. Price, $2.00. New York City: McGraw Publishing Co.

UNITED STATES LIGHTHOUSE BOARD. Reports on use of acetylene gas by the Canadian Government as an illuminant for aids to navigation. 26 pages; illustrated. 5 cents. Superintendent of Documents.

THETA-PHI DIAGRAM. Practically applied to steam, gas, oil and air engines. By Henry A. Golding. Second revised and enlarged edition. 126 pages; 48 illustrations. Price, $1.25. New York City: D. Van Nostrand Co.

MASSACHUSETTS STATISTICS OF LABOR. Bureau of Manufactures, Massachusetts and other States. No. 2 (in Labor Bulletin No. 49), 1907. Bureau of Statistics of Labor, State House, Boston, Mass.

TECHNOLOGICAL DICTIONARY. In the English, Spanish, German and French languages. By A. C. Huelin. 609 pages. Price, $4.00. New York City: Spon & Chamberlain.

BOOK REVIEWS.

METALL-ANALYSE AUF ELECTROCHEMISCHEM WEGE. By Dr. A. Hollard and L. Bertiaux. Authorized German translation by F. Warschauer. 125 pages. Price, bound, marks 6 (retail price in New York, $2.00). Berlin: M. Krayn.

It is always a praiseworthy undertaking for a chemical engineer to publish the results of his experience of years of practical work. It is especially praiseworthy if such a publication is not made in the special interests of the company with which he is connected. This praise is due to the authors of this work, which has been carefully translated into German by Dr. Warschauer, of Berlin.

The book consists of four parts, of which the first one is devoted to the principles of electro-analysis and classification of metals, while in the other parts the analysis of different metals and metallurgical products is specially discussed. The authors repeatedly call attention to the importance of the form of the electrodes for obtaining exact results, since the form of the electrodes is of influence on the distribution of the current density and on the diffusion phenomena. In general these two factors are not sufficiently taken into account, and especially chemists are inclined to think that the electric lines of force pass in straight paths from the points of the anode to the corresponding points of the cathode. This is only true in very special cases, for instance, when the electrolyte is contained in a cylinder and the top and the bottom cross-section of the cylinder form the two electrodes. In all other cases there is a stray field of lines of force as has been experimentally shown in the instructive paper of Mr. M. U. Schoop, published in one of the former volumes of this journal.

Of great interest is the chapter on the electrodes in which the constructions of Classen, Ribau and others are described, among them the platinum screen electrode of Hollard, which has the great advantage that speedy diffusion is rendered possible and that the phenomena occurring at the electrode may be observed by the eye during a test.

The book does not carry any unnecessary matter in form of long tables, etc. Every analytical chemist and even every electrochemist should find something useful in the book, and will pardon the German publisher for the fact that some pictures (for instance, Figs. 6 and 8) remind one of wood cuts in Bibles of the 17th century.

* * *

THE COPPER MINES OF THE WORLD. By Walter Harvey Weed. 375 pages; 159 illustrations. Price, $4.00. New York: Hill Publishing Co.

The tremendous advance in the mining and treatment of copper ores is concommittant with the rise of the electrical industry. Much attention to the metallurgical question has been given in the technical press, while the nature of mineral deposits that make copper mines has not been summarized in any book. To fill this known vacuum in technology is the purpose of this book.

The author, Mr. Weed, is well known for his work on the Geological Survey. Lately he has received deserved recognition from the captains of industry and has been retained by several large corporations as consulting geologist. This has given him an insight into commercial conditions. The benefit of this experience is seen in the comprehensive nature of this work, for it not only treats of the science but always exhibits the commercial instinct. As a "mine" should connote the words "business success," we believe that this is a laudable mingling of the two elements of applied science.

The book is "confessedly a compilation." It further exhibits marks of haste in preparation. The geology of copper deposits has been often described by men who were frank adherents of the school of "lateral secretion by surface or meteoric waters." This has been rudely disturbed of late by evidences of "secondary enrichment" in Butte in the shape of large bodies of phe-

nomenally rich ore at the 1,600, 2,000 and 2,400 feet level. It is inconceivable to any observer that this could have been effected by surface waters.

The more modern theory taken up by the school of younger geologists, to which the author belongs, is that of "expiring vulcanism." It attributes the formation of sulphide ores to the action of heated gases or solutions under pressure coming from the central part of the globe, the so-called "barosphere" and "secondary enrichment," in main, to the surging of these agents through an already formed deposit of low-grade ore catching up the copper from the heated portion and precipitating it in a cooler portion. Obviously this cooler portion might be at some depth.

The author usually seems to adopt this theory, though as it is in the transformation stage, his writings are colored at times by the old theories. For instance, on page 46, lines 16 to 20, he expresses the older theory without, however, the adjective "surface" or "meteoric," while on page 30, lines 3-5, he states that the occurrence of deposits of [rich] enargite at depths of 2,000 feet is opposed to the fact that enargite is secondary ore. On pages 54 and 55, however, he clearly states the genesis of ore deposits, allowing secondary enrichment by later igneous hydrothermal activity a much more prominent part.

Again on page 70 in the classification of ore deposits he places the Sudbury copper-nickel deposits as "segregations from basic igneous rocks." The term "segregation" is a wide one, and may mean either separation the way matte and slag are separated or a segregation by hydrothermal activity. We could wish the author had been less like the oracle at Delphi in this. Mr. D. H. Browne was of the opinion that the first hypothesis was the correct one. On the other hand, it would seem that the microscopic work of Kemp and his pupils has given importance to the latter ideas, though Prof. Kemp is not at all positive in his declarations.

However, it would be idle to criticize too much a book so excellent whose faults are due chiefly to the fact that economic geology is a most stubborn and unsatisfactory science. As Mr. Weed says, "facts are facts," to be used, to be studied, and to be studied and used again. This book presents chiefly facts and allows the reader to dig out his theories.

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CONTRIBUTIONS TO ECONOMIC GEOLOGY, 1906.—Part I.: Metals and nonmetals, except fuels. By C. F. Emmons and E. C. Eckels. 510 pages. Washington: Department of the Interior, U. S. Geological Survey, Bulletin No. 315. Series A, Economic Geology, 95.

This is the fifth of a series of bulletins of the U. S. Geological Survey, entitled "Contributions to Economic Geology." For the first time this bulletin has been divided into two parts, as a result of the division of the former section of iron ores and non-metallic minerals, Mr. M. R. Campbell being placed in charge of a new section devoted to the investigation of fuels, including coal, oil, gas and asphalts, and Mr. E. C. Eckel remaining in charge of investigations of iron ores, structural materials and miscellaneous non-metals. This change in the Survey organization has been used as a basis for a separation of the economic bulletin based on subjects. The present bulletin covers the work of the Survey in 1906 in metals, structural materials and other non-metals, except fuels. A separate bulletin will be issued later, covering Survey work on coal, lignite and peat.

Besides summaries of the work of the Survey in 1906 with respect to metalliferous ores, iron ores and structural materials, reports are given on gold and silver in Colorado, Montana, Washington and Wyoming; copper in Wyoming; nickel in Colorado, Maine, Oregon; iron and manganese ores in Alabama, Pennsylvania, Wyoming; aluminium and bauxite in New Mexico; Portland cement in Iowa and Wyoming; limestone in Alabama; gypsum in New Mexico; clays in Alabama.

Colorado, New Mexico, Georgia, Missouri, Pennsylvania; building stone and road metal in New England; glass sand in Indiana, Kentucky, Ohio and elsewhere; quartz and feldspar in Maine, New York; mica in North Carolina and Wyoming; graphite in Wyoming; mineral paint ores in Pennsylvania (and an article by E. F. Burchard, on Southern red hematite as an ingredient of metallic paint); abrasive materials in California; phosphorus ore in Western United States, Arkansas, Pennsylvania; sulphur in Utah.

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GYPSUM AND GYPSUM PRODUCTS IN 1906. By Ernest F. Burchard. Washington: Department of the Interior, United States Geological Survey.

This pamphlet of 14 pages is an advance chapter from *Mineral Resources of the United States* for 1906. The first parts discuss the character of gypsum with analyses, the range and distribution of gypsum, uses of gypsum and the chemistry and practice of gypsum burning and the making of plaster of paris. After a review of the condition of the trade, statistical tables are given on the production in the United States and other countries. The gypsum mined in the United States in 1906 amounted to 1,540,585 short tons, valued at $1,147,129. This production represents an increase in quantity of more than 47 per cent, and in value of nearly 40 per cent, as compared with that of 1905.

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LABORATORIUMSBUCH FÜR DEN EISENHÜTTEN CHEMIKER. By Max Orthey. 49 pages. Price, mark, 1.80 (retail price in New York, 60 cents). Halle a. S.: Wilhelm Knapp.

This little book is Part I. of a series of fourteen laboratoriumsbücher which are to deal in a brief and practical manner with the different branches of technical analytical chemistry. The book contains schemes for the "sufficiently exact" determination of the constituents of iron ores, iron and steel, slags, limestone, refractory materials, fuels and gases.

A few samples of the methods are as follows: Silicon in pig iron is determined by dissolving in hydrochloric acid, evaporating to dryness, redissolving, filtering and weighing as SiO_2, regardless of the titanic acid often present. The nitric and sulphuric acid method used in this country is fully as rapid and is free from this serious source of error. Carbon is determined by solution in copper ammonium chloride with combustion of the carbon residue in chromic and sulphuric acids.

In determining phosphorus 1 gram of iron is dissolved in nitric acid, transferred to a porcelain dish and evaporated to dryness on a sand bath. Phosphorus is peroxidized by roasting one-half hour over a Bunsen flame. The residue is then treated as an iron ore.

While there is much that is interesting in this work, it is not probable that the methods proposed will find favor with American iron chemists.

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TRANSACTIONS OF THE FARADAY SOCIETY. Vol. III., Part 1., 102 pages; illustrated. Price, 10s. 6d. London: The Faraday Society.

This issue is introduced by a highly theoretical paper of E. E. Fournier-d'Albe on the application of the electron theory to electrolysis, followed by an interesting symposium of papers on osmotic pressure with an extended discussion of the subject. The Earl of Berkeley discusses the direct measurement of osmotic pressure, Mr. W. C. Dampier Whetham indirect methods of measuring osmotic pressure, Dr. T. Martin Lowry the osmotic pressure from the standpoint of the kinetic theory, Dr. L. Kahlenberg (University of Wisconsin) the bearing of actual osmotic experiments upon the conception of the nature of solutions. The chief points brought out in this discussion have already been covered in our columns.

The second half of the book consists of more or less

theoretical papers by H. Nutton and H. D. Law on the potential of hydrogen liberated from metallic surfaces, by F. M. G. Johnson and N. T. M. Wilsmore, on electrode potentials in liquid ammonia, by J. G. A. Rhodin on the impedance of solutes in solvents as manifested by osmotic "pressure," and by T. S. Price on the electrolytic deposition of zinc, using rotating electrodes.

Sandwiched in between these sets of scientific papers—many of which are of considerable intrinsic value—we find a commercial paper by J. B. C. Kershaw on the present position and future prospects of the electrolytic alkali and bleach industry. This industry is now so important that a thoroughly up-to-date and reliable review of it would be very valuable. But it seems impossible to prepare such a review at present. Mr. Kershaw's statistical figures are to the largest part confessedly not authoritative; in his opening remarks he regrets "the excessive modesty of electrochemical firms about their achievements, or the objection there is on the part of manufacturers to allow the world to know what is being done and what progress is being made."

Mr. Kershaw's paper begins with historical notes, mostly relating to early history; then follow statistical tables of the different companies in different countries working electrolytic alkali processes. with more or less incomplete data as to equipment. How far the data are exact or up to date may perhaps be judged from the notes on three of the six American companies noticed. No. 26, the Pennsylvania Salt Co., is stated to work the Bell Bros. mercury process at Wyandotte; this is ancient history; this process has indeed been used there on an experimental scale, but has long since been abandoned. Under No. 27, the works of the Roberts Chemical Co., at Niagara Falls, are reported "to have been burnt down recently." This has happened in August or September, 1905, but thy have been rebuilt soon afterwards and have since been in working order. The reverse is the case with No. 28, the Acker Process Co., at Niagara Falls; these works burnt down this Spring and have not been rebuilt, so that there exists no longer any industrial process electrolyzing fused salt for chlorine and caustic production. Mr. Kershaw cannot be blamed, however, for stating this process as one in operation, since the fire occurred after his paper had been read. It is also stated that "a new works, using the Townsend diaphragm cell, is about to be started in Niagara Falls"; this plant has been in commercial operation for more than a year and a half. There are other smaller inaccuracies; for instance, Mr. Kershaw wants to restrict his notes to "electrolytic alkali works," but gives in his tables, nevertheless, the works of the Dow Chemical Co., in Midland, Mich., which do not make caustic. It is to be hoped that the data on European plants—incomplete as they confessedly are— are more correct. But it is suspicious that no mention is made of the inroads which the Glocken process is now making in German plants.

The paper is concluded by interesting remarks on the probable future of the electrolytic industry. In these the author seems to be more fortunate than in his statistics. His conclusions given here are practically identical with those given by himself in an article in ELECTROCHEMICAL AND METALLURGICAL INDUSTRY, Vol. IV., p. 173.

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OPEN-HEARTH STEEL CASTINGS. By W. M. Carr. 118 pages; 19 illustrations. Price, $1.50. Cleveland: The Penton Publishing Co.

This little book is compiled from a series of articles by the author, published in *The Iron Trade Review* and *The Foundry*. It will be found a useful and quite complete summary of the chief points which require attention in the manufacture of open-hearth steel castings, both by the basic and acid process. The book is practical and fully up to date; thus, the eleventh chapter gives an exposition of the repair of steel castings by the thermit process.